Wettability of hair using natural and synthetic surfactants in presence of silver nanoparticles as additive

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Thesis Submitted by

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CERTIFICATE

This is to certify that the thesis entitled "**Wettability of hair using natural and synthetic surfactants in presence of silver nanoparticles as additive"** submitted by Krishnendu Chatterjee in partial fulfillments for the requirements for the award of Master of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree.

Date-26/05/2012

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Date-26/05/2012 **Krishnendu Chatterjee**

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ABSTRACT

Synthetic surfactants are used for various industrial purposes ranging from surface cleaning, oil recovery, froth floatation, etc. The synthetic surfactants are not easily biodegradable and are quite costly, leaving surfactants extracted from microbial and plant as possible alternative sources to it. Plant surfactants on the other hand are cheaper and also suitable for mass production compared to surfactants extracted from microbial source, but it has inferior wetting and surface tension properties compared to synthetic surfactant. So, silver nanoparticle was used as an additive, as it has antimicrobial properties and also increases the wetting property of the surfactant. This report mainly focuses on the wetting property of pure surfactant system on hair as well as the growth kinetics of silver nanoparticle in acacia solution and its effect on wettability of hair. The objective of this study is to obtain insight into the wetting behaviour of human hair in presence of three plant surfactants, namely reetha, acacia and shikakai and also along with silver nanoparticles synthesized in-situ in acacia extract.

***Key Words*:** Plant surfactant, Wettability of hair, Nanofluid wetting behaviour, Silver nanoparticle synthesis in Acacia, Reetha and Shikakai medium.

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NOMENCLATURE

CA	Contact Angle
CMC	Critical Micellar Concentration
PTFE	Polytetrafluoroethylene
PMMA	Polymethylmethacrylate
CTAB	Cetyltrimethylammonium bromide
CPYB	Cetylpyridinium bromide
EDMAB	Dodecylethyldimethylammonium bromide
BDDAB	Benzyldimethyl dodecylammonium bromide
TX-100	TritonX-100
Span20	Sorbitan monolaurate
Tween 20	Polyoxyethylene(20) sorbitan monolaurate
PFC	Perfluorocarbon
IO	Indium oxide
ALS	Ammonium lauryl sulphate
SLS	Sodium laureth sulphate
SKC	Stearalkonium chloride
BKC	Benzalkonium chloride
SEM	Scanning electron microscope
XRD	X-ray diffraction
DLS	Dynamic light scattering
OCA	Optical contact angle
DCA	Dynamic contact angle

LIST OF SYMBOLS

γ	Surface tension
τ	Surface excess
θ	Contact angle
γ_{SV}	Interfacial tension between solid and air
γ_{SL}	Interfacial tension between solid and liquid
γ_{LV}	Interfacial tension between liquid and air
τ_{SG}	Surface excess between solid and gas
τ_{SL}	Surface excess between solid and liquid
τ_{LG}	Surface excess between liquid and gas
W_A	Work of adhesion
N	no of electrons in the plasma;
e	change of an electron;
m_e	effective mass of electron;
ω_p	oscillating frequency.

Chapter 1

INTRODUCTION

1. INTRODUCTION

1.1 Importance of surfactants

Wetting is the phenomenon of spreading of liquid droplet on solid surface. Wettability of a solid principally depends upon the concentration and composition of the surfactant solution along with the nature of the solid substance [Szymczyk and Janczuk., 2008]. A large number of industrial fields such as froth flotation [Fraunholcz, 2003], oil recovery [Churaev et al., 2001], oil agglomeration [Garcia et al., 1998], surface cleaning, coating [Swarup and Schoff, 1993], printing [Xue et al., 2006], adhesion and detergency demand a basic understanding of the wetting process, and the parameters affecting it. The explanation of various forces like van der Waals interactions, interfacial free energy, spreading and capillary flow phenomena becomes lucid by knowing the wetting and dewetting properties of surfaces [Xia et al., 2001]. The significance of surfactants has also increased numerous folds in cosmetic industry, where it is primarily used as wetting agents, conditioners, cleanser, solubilizers, etc. Shampoos, shower gels and soaps consist of mainly anionic surfactants along with its salt, whereas the bulk composition of conditioners comprises of cationic surfactants.

1.2 Wettability and Contact angle

Contact angle (CA) is the angle between the solid-liquid and liquid-air interface.

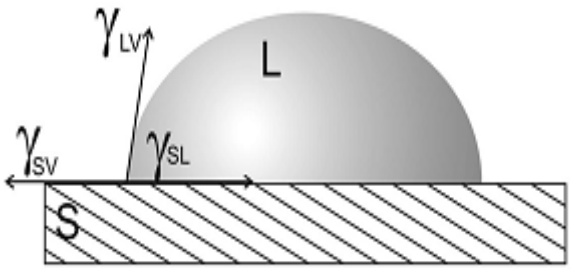


Figure1.1: Diagrammatic representation of wetting phenomenon (Young's equation).

$\gamma_{LV} \cos\theta = (\gamma_{SV} - \gamma_{SL})$

θ = contact angle;

γ_{SV} = Interfacial tension between solid and air;

γ_{SL} = Interfacial tension between solid and liquid;

γ_{LV} = Interfacial tension between liquid and air;

Interfacial tension or surface tension is defined as the force needed to oppose the natural pull of the molecules in the surface or interface to increase in area of surface or interface.

Contact angle gives the measure of wettability of a solid surface. When contact angle is 0°, it said to be complete wetting i.e, solid has strong affinity towards the liquid and when contact angle is 180°, it is said to be non-wetting, i.e, solid has no affinity towards liquid. But these are ideal cases and are not found in nature, whereas in actual contact angle lies between 0° and 180°.

The solid surface can be broadly classified into two types-hydrophilic and hydrophobic, depending upon the amount of wetting facilitated by them.

Hydrophilic surface means the solid surface that has an affinity towards water. Water spreads very well upon this solid surface typically giving a contact angle less than 90°. Since contact angle is less, the exposed area of liquid to air is less, thus surfaces have lower surface energy because of lower surface area. Glass is an example of hydrophilic surface.

But on the other hand water does not spread well enough on hydrophobic surfaces and contact angle is over 90°. Consequently, surfaces have higher surface energy because of higher surface area. Teflon is an example of such a type of surface.

1.3 Effect of surfactants on wettability

Surfactant represents a heterogeneous and long-chain molecule containing both hydrophilic (head group) and hydrophobic moieties (tail). When surfactant molecules are introduced to the liquid, the surfactant molecules along with the solvent molecules are oriented in a manner so as to minimize the entropy Adsorption of surfactant is the process where surfactant molecules accumulate at the interface from the bulk solution, lowering the overall free energy of the system. Surfactant concentration increases on the addition of more and more surfactant molecules and surface tension goes on decreasing till CMC is reached.

The surfactants are broadly classified into cationic, anionic, non-ionic and zwitterionic depending upon the charge of head group attached to the surfactant molecule. When the head group is negatively charged, the surfactant is called anionic and if positively charged it is

called cationic surfactant. Head group is neutral in case of non-ionic ones. Zwitterionic surfactants carry both the charges and behave as cationic, anionic and non-ionic depending upon pH of solvent, temperature, concentration and other conditions.

Plant surfactants are biocompatible, nontoxic and nonionic, thus proving an attractive alternative to synthetic surfactants, which generally fail to comply with the environmental safety standards. Reetha (*Sapindus mukorossi*), shikakai (*Acacia concinna*) and acacia (*Acacia auriculiformis*) which are common to S. E. Asia, has been traditionally used as shampoo and detergent agents. The surfactant is extractable in pure form and has shown useful properties like medicinal properties, increased degradability, reducing property, etc. The plant surfactant being environmental friendly provides an alternative green route for nanoparticle synthesis also.

1.4 Biogenic synthesis of silver nanoparticle

Biosynthesis of nanoparticles has received considerable attention due to the growing need to develop environmentally benign technologies in material synthesis. The development of reliable green process for the synthesis of silver nanoparticles is an important aspect of current nanotechnology research, since silver has antimicrobial properties. Nanoparticles are used for the preparations of compounds like drugs, vitamins, steroids, proteins, flavours, etc. The purposes of using nanoparticles include protection, prolonged activity, controlled release and improved rheological properties. Nanoscale inorganic particles have unique properties such as catalytic, optical, magnetic and electrical. Chemical reduction, photochemical reduction, electrochemical reduction, heat evaporation, etc., chemical and physical methods are used for nanoparticle synthesis, which are not environmentally friendly. Here, we have presented a simple and environmental friendly route for the synthesis of silver nanoparticle from silver nitrate salt by utilizing the fruit extract of *Acacia auriculiformis* (green synthesis) and compared its properties with silver nanoparticle formed by reducing aqueous silver nitrate using a strong reducing agent, sodium borohydride (chemical synthesis), in surfactant medium (reetha and shikakai).

Chapter 2

BACKGROUND LITERATURE

2.1.Introduction

Amphiphilicity is the special property of surfactants, which makes them suitable for myriad applications like detergency, froth floatation, oil recovery, wetting, etc. Among which wetting of solids has generated immense interest among the researchers owing to its significant role in practical fields like lubrication, floatation and other utilities in daily life. The wettability of a material by a given fluid can be improved by either manipulating the surface through coating or by the application of nanoparticles in fluid suspension (nanofluids). The coating of surfaces also play a major role in preventing adhesion and improving wettability, which finds application in, polymer industry, material processing etc. The wettability of pure surfactants has been widely studied on various surfaces, to improve and meet diverse application requirements. But the prevailing needs to improve the wettability on surfaces, where surface coating is not feasible; has led to the addition of nanoparticles in the fluid, which enhances wetting behaviour.

2.2.Wettability of surfactants on flat surfaces

Extensive research has been performed on solution behaviour and contact angle studies for surfactant systems. The studies on wetting behaviour of hydrophilic and hydrophobic surfaces have been widespread. The wettability of hydrophobic surfaces is generally improved by surfactant solutions. Among the earlier works the effect of nonionic (ethoxylated nonyl phenol and ethoxylated dodecyl ether type) surfactants on hydrophilic (α-quartz) and hydrophobic (siloxanated and silanated α-quartz) plates on contact angle was studied way back by Scales et al., (1986). The wettability of hydrophobic surfaces like PTFE (polytetrafluoroethylene) and PMMA (polymethyl methacrylate) using cationic surfactant mixtures of CTAB (cetyltrimethylammonium bromide) and CPYB (cetylpyridinium bromide) [Szymczyk et al., 2006], non-ionic Triton X-100 and and short chain alcohol mixtures (Zdziennicka. 2009), C_{12} (EDMAB) (dodecylethyldimethylammonium bromide) and BDDAB (benzyldimethyl dodecylammonium bromide) [Harkot and Jan´czuk, 2009] has been done. The trend followed by surface tension and contact angle due to addition of cationic surfactant on teflon surface was studied by Harkot and Jan´czuk (figure-2.1) (2009).

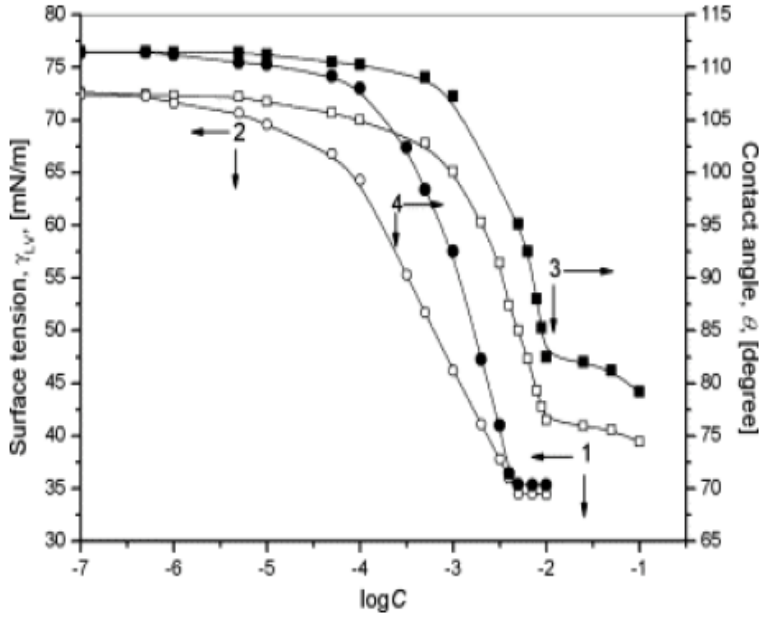


Figure-2.1: The relationship between the values of the surface tension (γ_{LV}) of aqueous C_{12}(EDMAB) (□) and BDDAB (○) solutions and the values of the contact angle (θ) of aqueous C_{12}(EDMAB) (■) and BDDAB (●) solutions for the PTFE surface and the concentration of the surfactants (log C) [Harkot and Janczuk, 2009].

Wang and his fellow workers illustrated the important parameters causing the variation in data which is in the order of surface hydrophobicity > initial impact velocity > surfactant on wetting diameter and surface hydrophobicity ≈ initial impact velocity > surfactant on droplet height [Wang et al., 2009].

It is interesting to note here that contact angle is controlled by surface tension for common linear surfactants but becomes independent of surfactant concentration C_s as the value of C_s >critical micelle concentration for superhydrophobic surfaces [Chang et al., 2007]. The wetting behaviour of superhydrophilic [Piispanen and Hupa, 2011; Fangfang et al., 2011] and superhydrophobic surfaces [Lee et al., 2011; Mohammadi et al., 2004] have also been explored by various groups of researchers.

Nonionic surfactants are advantageous in a diversified range of applications because of their low CMC and surface tension values over the ionic surfactants. Nonionic surfactants, in general, are very useful in mixed surfactant systems because of their electrical neutrality. The adsorption and wetting behavior of two nonionic surfactants (TX-100 and Igepal CO-630) having the same head group but structurally different tail groups has been studied by Biswal and Paria [Biswal and Paria, 2011].

2.3.Wettability of surfactants on fibre and hair

The wettability of surfactant on fibre plays a significant role in the textile industry (self-cleaning fabric), polymer composites engineering and the cosmetic industry (shampoo, conditioners, etc) among others. The wetting property of the droplet controls the geometry of a droplet on fibre. It is interesting to note that the wetting shape of a microdroplet on a fiber does not appear as a partial sphere as that on a flat surface. The Welhelmy balance technique has been commonly employed for measuring the contact angle of individual fibers. It is interesting to note here that the drop diameter plays a vital role in determining the exact contact angle, since if the drop diameter is much larger than that of the fiber, then the measured contact angle becomes misleading. In the textile industry, the cleaning and waterproofing property of the surfactant along with the nature of fiber dyeing is mainly considered whereas interfacial properties of fiber/ matrix and their bonding strength at the interface is the focus of study in polymer composites engineering. While, Zhu, L, et al., (2006), studied the wetting properties of thermally bonded polyester nonwoven fabrics with different basis of weights, Wu, X.F, et al., (2006) gave a theoretical basis of determining surface tension of fluids based on a sessile drop on a fiber. These methods could prove to be invaluable in understanding of the wettability of fluid droplets on filaments, extensively used in the textile industry and fiber/epoxy composites engineering.

The contact angle of any sessile drop on a mat of fibers or on woven fabric is much different than the contact angle on an individual fiber of the same material. For this reason, comparisons can only be possible for fabrics with the same pore structure and size, a feat quite difficult to achieve. The difference in contact angle occurs due to the position of fibers which changes the three-phase contact line. Also, adequate care must be taken to ensure that preferential adsorption of any liquid doesn't occur on the fibre. This makes it all the more difficult to predict and interpret the contact angle values of different liquids on individual fiber as well as on fiber bundles. Among the works available on wettability of fiber-bundle, Kim and Hsieh, studied the wetting and adsorbency of two nonionic surfactants, sorbitan monolaurate (Span20) and polyoxyethylene(20) sorbitan monolaurate (Tween 20) on cotton fabrics (figure-2.2) [Kim and Hsieh, 2001].

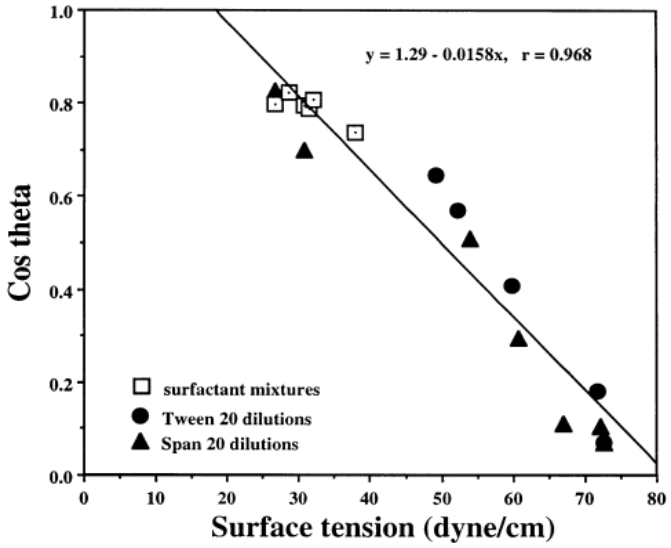


Figure-2.2: Relationship between cos θ and surface tension of all surfactant systems: Mixture, Span 20, Tween 20 [Kim and Hsieh, 2001].

The need of improving look and quality of hair has created a huge industry based on hair-care products. Wettability plays an important part in increasing this efficiency. The wettability of hair thus demands an intensive study to improve product performance. The variation in hair quality from person to person makes it difficult to characterize the wettability of hair, with accuracy and repeatability. Kamath et al., (1984) was among the early group of researchers, who studied the wetting forces of cationic surfactant (stearyldirnethyl-benzylammonium chloride) on individual human hair fiber, by Wilhelmy measurement technique. Khenniche et al., (2003) and Lodge et al., (2006) performed a great deal of research to co-relate between wettability of hair and hair condition. The contact angle of pure water on Caucasian hair was found to be 98.3° [Khenniche et al., 2003] and 103±4° [Lodge et al., 2006], respectively. Lodge et al., (2006) worked with both untreated and treated hair belonging to Caucasian group of people along with hair samples of Asian and African people, concluding that the wetting behaviour of hair depends on the hair condition itself (figure-2.3) rather than on the ethnicity of the group (figure-2.4). The apparent problem however lies in fact that the small depth of immersion in the fluid makes it problematic to obtain results accurately. By studying the results we can conclude safely that the wettability of hair depends primarily on the condition of the hair surface rather than on the ethnicity of the group from which the hair was obtained. The wettability of damaged hair or treated hair is comparatively more than virgin hair, since the cuticular cover of the hair is dented making it porous, thus allowing better absorption in the process.

Table-2.1: Summary of Average Advancing Contact Angle Values of pure water on hair strand [Lodge et al., 2006].

Sample	Contact angle (°)	
	Dry	Soaked
Virgin	103 ± 4	98 ± 2
Virgin treated	88 ± 9	92 ± 1
Chemically damaged	70 ± 7	70 ± 8
Chemically damaged treated (one cycle)	79 ± 1	84 ± 2
Chemically damaged treated (three cycles)	77 ± 5	72 ± 4
Asian	95 ± 4	–
African	92 ± 11	–
Mechanically damaged	80 ± 14	–
Virgin—with scale (WS) orientation	85 ± 10	–

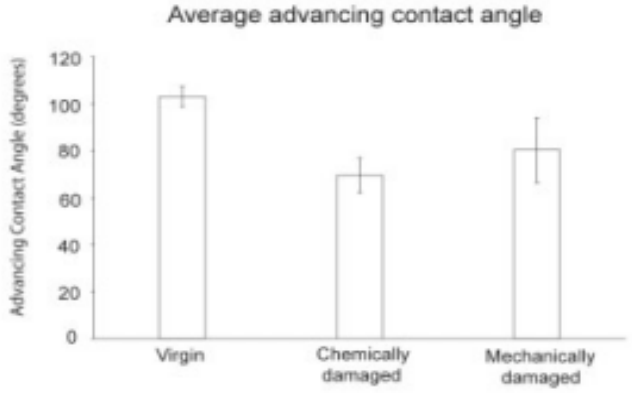


Figure-2.3: Average advancing contact angle comparing chemical and mechanical damage effects [Lodge et al., 2006].

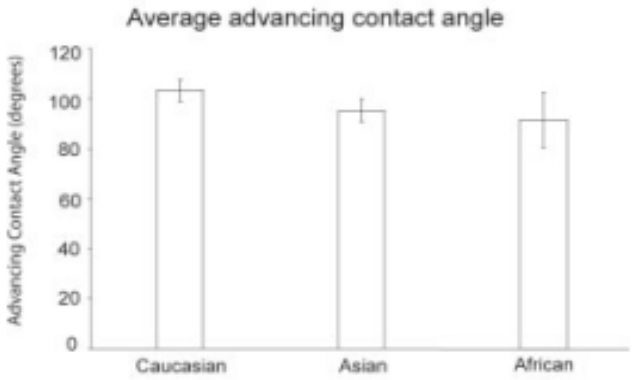


Figure-2.4: Average advancing contact angle values showing ethnicity dependence. No significant dependence on ethnicity was found for advancing contact angle values [Lodge et al., 2006].

Table-2.2: Previous wettability studies of surfactants on fibre and hair.

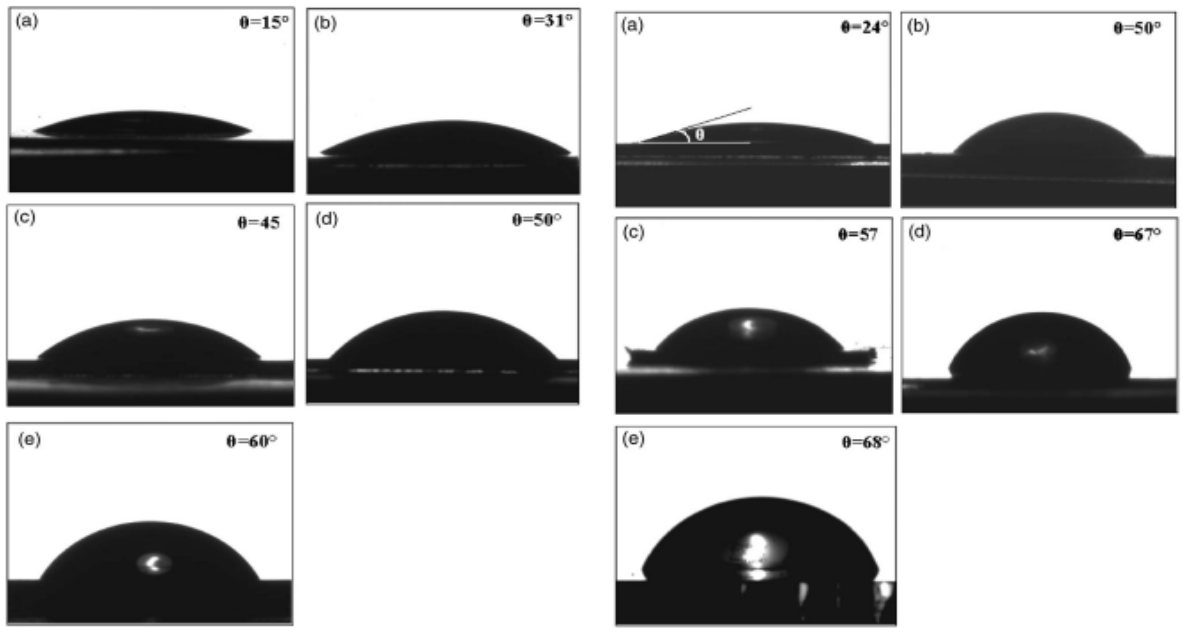
Paper Title	Work Done	Reference
Marangoni Effect in the Water Wetting of Surfactant Coated Human Hair Fibers	Individual human hair fibers treated with a cationic surfactant (stearyldirnethylbenzylammonium chloride)	Kamath, Y. K, et al., J Colloid Interf. Sci., 1984.
Wetting Properties of Human Hair by Means of Dynamic Contact Angle Measurement	Wettability of hair, and effect of hair care products on wetting properties	Lodge, R.A, et al., J. Appl Polym. Sci., 2006.
Scalp hair: a model for the evaluation of cosmetic formulations intended for depilation	Work of adhesion (W_a) estimation using wettability measurements for depilatory wax and leg hair	Khenniche, S, et al., Polym. Int., 2003.
Droplet on a fiber: geometrical shape and contact angle	The geometrical shape, wetting length, and contact angle of microdroplet on a fiber was studied.	Wu, X.F, et al., Acta Mechanica, 2006.
Wetting Behavior of Thermally Bonded Polyester Nonwoven Fabrics: The Importance of Porosity	Wetting properties of thermally bondedpolyester nonwoven fabrics with different basis weights were studied.	Zhu, L, et al., J. Appl Polym. Sci., 2006.
Wetting and absorbency of nonionic surfactant solutions on cotton fabrics	The effects of changing aqueous solution properties by nonionic surfactants on the wetting and absorbency in cotton fabrics was observed	Kim, C; et al., Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2001.

The main purpose of this study is to obtain an insight into the wetting behaviour of human hair in presence of three plant surfactants, namely reetha, acacia and shikakai, which are cheap, environmental friendly, commonly used surfactants for washing of hair. Silver

nanoparticles synthesized in-situ in acacia extract and ex-situ by reduction of aqueous silver nitrate by sodium borohydride (chemical synthesis), in surfactant medium (reetha and shikakai), were also used for checking the wetting properties of the nanofluid on hair. Besides it has been observed that the nanofluid has increased wetting as well as antimicrobial properties, which is considerably more than in its purer form.

2.4.Wetting behaviour of nanofluid

Nanocoatings of surfaces can modify properties of the surface like roughness and surface energy. Sobac and Brutin (2011), used five fluids (methanol, ethanol, propanol, toluene and water) under normal atmospheric condition on aluminium coated surfaces (perfluorocarbon (PFC), polytetrafluoroethylene (PTFE), SiOC and SiO_x), to study the effects of drop evaporation. The range of wettability extended from 17° to 135°, indicating modification of surfaces can play a key role in making surfaces either hydrophobic or hydrophilic in nature. Besides surface energy surface roughness and nanoparticle distribution, can also play an important role to control contact angle changes.



(A) (B)

Figure-2.5: (A) Images of water droplet on IO nanoparticles having sizes of (a) 14 nm, (b) 87 nm, (c) 210 nm, and (d) 620 nm, and of (e) IO thin film. (B) Images of DEG droplet on IO nanoparticles having sizes (a) 14 nm, (b) 87 nm, (c) 210 nm, (d) 620 nm, and on (e) IO thin film, respectively [Munshi et al., 2008].

Experimental and theoretical analysis, conducted by Munshi et al., (2008) established the fact that with the increase in indium oxide (IO) nanoparticle size coated on the surface of a material (alumina), the contact angle increases for a given fluid (water or diethylene glycol), thus wetting decreases. This phenomenon can be attributed to the fact that the surface to volume ratio is more for small nanoparticle compared to larger nanoparticle; thus smaller nanoparticles have larger surface energy, which decreases contact angle and improves wettability (figure-2.5).

An alternative way to improve wettability of the surface, where coating is not appropriate can be done by the use of nanoparticle suspended in fluids (nanofluid). The wetting behaviour of nanofluid is more than the wetting behaviour of the fluid (without nanoparticle) by itself on a given surface. The effect of nanoparticles on surface tension and contact angle has been an important topic of research in the field of surface and colloid sciences for nearly a decade now [Vafaei et al., 2011; Sefiane et al., 2008; Chaudhury, M.K, 2003; Rao, Y, 2010, Wasan and Nikolov, 2003]. Nanofluids have found applications in magnetic resonance imaging (MRI) [Ai et al., 2005], drug delivery vehicles [Nasongkla et al., 2006], hyperthermia therapy [Grainger and Castner, 2008; Ma and Liu, 2007], coolants [Eastman et al., 2001] and cosmetic industry. The addition of nanoparticles increases the thermal conductivity and viscosity of nanofluids considerably over the base fluid. The use of nanofluids reduces effects of sedimentation, erosion of pipes and agglomeration, making them quite attractive for heat transfer applications. Nanofluids containing surfactant micelles can prove to be valuable for soil remediation, oily soil removal, improved oil recovery, detergency, lubrication, etc, owing to its enhanced spreadability.

The presence of nanoparticles has been known to reduce the contact angle and improve wettability. The addition of even small amounts of nanoparticles in the base fluid gives rise to distinct “stick-slip” pinning behaviour of the triple line contact angle. The increase in nanoparticle concentration increased the “stick-slip” behaviour of the nanofluid. The accumulation of nanoparticle near the three-phase contact angle, caused due to the advective flow is mainly responsible for the given effects. Moffat et al., (2009) studied the changes in the concomitant behaviour in (de)wetting and evaporation of sessile drops for both pure ethanol and the by adding TiO_2 nanoparticles. Kondiparty et al., (2010) found out experimentally that the deformation of fluid wedge tip occurs under the action of structural film disjoining pressure, which develops in thin liquid film (less than 10 nm thick) when its two surfaces attract or repel each other through van der Waals and electrostatic forces. The

disparity amongst van der Waals and electrostatic forces causes fluid flow towards or away from the wedge tip; hence causing wetting or dewetting, depending upon the flow. Thus, capillary and disjoining pressure are of paramount significance for establishing the stability of thin curved films. The structural film disjoining pressure is more towards the edge of the liquid film than at the centre, since disjoining pressure increases with the decrease in film thickness. Wasan et al., (2011) also applied the concept of the structural disjoining pressure gradient or film tension gradient to explain the spreading of nanofluid. The observed film tension for a single layer of particle was also found to be higher than a two-layered particle.

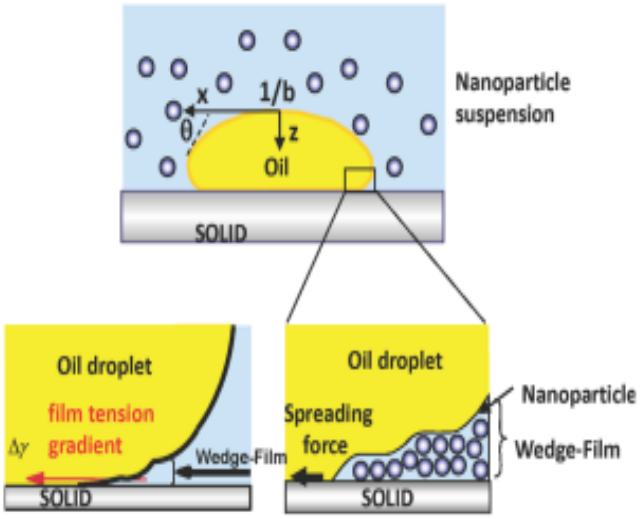


Figure-2.6: Nanoparticle structuring in the wedge- film resulting in structural disjoining pressure gradient/film tension gradient at the wedge vertex [Kondiparty et al., 2010].

From figure-2.6, it can clearly be seen that nanoparticles accumulate near the triple line (three-phase contact line) due to the phenomenon of advective flow, which drives the nanofluid to spread out at the wedge tip. The spreading is caused due to the increase in film tension which is always directed towards the wedge tip from the bulk solution. This film tension thus enhances the spreading of nanofluid which in turn aids dynamic spreading and improving wettability. Vafaei and co-workers (2006) demonstrated experimentally that with the increase in particle concentration the contact angle shows an increase before reaching a peak and then decreases.

Substrate material and particle size also influences the variations in contact angle as a function of concentration. For the same droplet volume and same mass concentration, smaller nanoparticles were more effective in raising the contact angle than their larger counterparts for hydrophilic surfaces. At any given concentration of nanofluid, the contact angle decreases

with an increase in nanoparticle size. So, enhanced spreading of the nanofluid can be achieved by using small sized nanoparticle and higher volume concentrations of the nanofluid. The degree of displacement of the three-phase contact line increased with an increase in the nanoparticle volume concentration as well as decreasing the size of the nanoparticle. The wettability of a given solid thus depends on a number of parameters including nanoparticle size, concentration used, type of surface, surfactant concentration among others.

2.5.Motivation of the project

Surfactants used for the cosmetic formulation has to pass a variety of tests before they are deemed fit to be deployed for human applications, which raises the cost considerably. Hair which is made up of 97% keratin protein, containing mostly negatively charged amino acids, is washed with shampoo to remove its dirt. Shampoo contains mostly anionic surfactants like Ammonium lauryl sulphate (ALS), Sodium laureth sulphate (SLS), etc which are more anionic than the amino acids of keratin, thus easily removing the dirt from hair. But, they also remove essential natural oils along with dirt. So, conditioners containing cationic surfactants like stearalkonium chloride (SKC), benzalkonium chloride (BKC) are used after shampoo wash as it does not completely rinse with water adding a thin film to hair, thus giving it wt and making it easier to comb. Otherwise the hair looks frizzy. Also, these surfactants are mostly of synthetic origin and pose a problem in disposal after its usage, since they are not biodegradable. The problem of degradation combined with the relative cost of synthetic surfactant has led researchers to focus on other alternative surfactant sources, which are both cheaper and environmental friendly. In this regard, surfactants extracted from microbial sources and plant sources have come in the limelight. The advantages of using plant surfactant over surfactant extracted from microbial sources are many folds, which include cheaper cost of production and extraction and also the huge quantity that can be produced in a given time period. Reetha, shikakai, etc has been used as shampoo while jojoba oil, heena, etc has been used as conditioner agents by the people of Indian sub-continent for a very long time, since they have been known to possess no significant side-effects, by virtue of being natural products. Surfactants are also known to create a variety of dispersed systems like suspensions, emulsions and also for the synthesis of nanoparticles. Surfactants extracted from plant have mild reducing and anti-microbial property, which has been exploited for the biosynthesis of silver nanoparticle, which plays a dual role of improving wettability and as an anti-microbial agent. Plant surfactants are prone to microbial attack and thus cannot be stored

in solution phase for long periods of time. The anti-microbial property of the silver nanoparticle helps in increasing the shelf life of the surfactants in the solution phase. Also, using additives also increases the wettability. Here Ag NP is used as additive. Following the shift of balance towards more eco-friendly methods, silver has also been synthesized from its salt by reducing it with surfactants, which act as mild reducing agent.

2.6. Objective of the project

The association between human hair and water occurs continuously in atmospheric air and also during the application of various hair care products. The main objective of the project is to check the wettability of hair, and how plant and synthetic surfactants affect the wetting properties.

1. To compare the wetting behaviour of virgin and treated human hair.
2. To compare the wetting behaviour of human hair in presence of three plant surfactants, namely reetha, acacia and shikakai with non-ionic surfactant Triton-X 100.
3. To know the growth kinetics of silver nanoparticle via green synthesis.
4. To know the effect of nanoparticle in plant surfactant medium on wettability of hair.
5. Characterization of silver using SEM, XRD, DLS.

Chapter 3

EXPERIMENTAL WORK

3.1. Materials:

Human hair of Caucasian origin was obtained from Indian volunteers for conducting the study. The natural surfactants used for wetting, were extracted from reetha (*Sapindus mukorossi*), shikakai (*Acacia concinna*) and acacia (*Acacia auriculiformis*). Extraction of saponin from reetha (MW-966) was done according to methodology followed by Kommalapati and co-workers (Kommalapati et al., 1997, Kommalapati et al., 1998). While saponin extraction from shikakai (MW-1056) was done according to the methods of Tezuka et al., 2000 and that of acacia (MW-1765) was done according to the works of Garai and Mahato, 1997, Pal et al., 2009, respectively. The only exception was that the extraction of saponin from acacia was done by di-ethyl ether (sd fiNE-cHEM LiMiTEd, 99%) and methanol (MERCK Chemicals, 99%) mixture (5:1), instead of chloroform-methanol (80: 20) followed by Garai and Mahato, 1997. Certified analytical grade ethanol (Hong Yang Chemicals Corp., China, 99.9%), sodium borohydride (Acros Organics, 98+%) and silver nitrate (MERCK Chemicals) were used. Ultrapure water (Sartorius, Göttingen, Germany) of 18.20 MΩ cm resistivity, 72.16 mN/m surface tension, and 6.5-7.0 pH was used for all the experiments.

Figure-3.1: Fruits of (A) acacia [*Acacia auriculiformis*] (B) shikakai [*Acacia concinna*] (C) reetha [*Sapindus mukorossi*].

3.2. Hair Sample Preparation

These studies were conducted on Indian black virgin hair (both male and female), without any chemical treatment. Nevertheless, prior to being used for the experimental work, each strand of hair was rinsed thoroughly with water, followed by ethanol and finally with water again, for reducing the amount of unwanted deposits which accumulate over the cuticle over a period of time. Then after each wash, individual hair strand was dried for 3 minutes, using an ordinary hot air blower. This procedure was repeated before each use for the dual purpose of curbing cuticular deposits as well as to maintain the dryness of hair, since due to its porosity it has the ability to retain some moisture from previous washes.

3.3. Measurement of surface tension and calculation of CMC

The solution preparation was done moments before the actual measurement. The solutions of the desired concentration (0.001-1 mmol/L) were prepared from 5 mmol/L stock solution, using 50 mL volumetric flask. For measuring surface tension a surface tensiometer, (DataPhysics, Filderstadt, Germany, DCAT-11EC) was used. Platinum sheet is used for surface tension measurement in Wilhelmy plate technique.

Figure 3.2: Photograph of surface tensiometer.

To avoid the adsorption of surfactant on the plate it was cleaned properly with ethyl alcohol and water and was also burned in alcohol flame to ensure a clean surface, after each measurement. During the experiment, the temperature was maintained constant at 25 ± 0.5 °C with the help of a circulator. The immersion depth of the platinum plate in the surfactant solution was maintained at 3 mm. The CMCs of reetha, shikakai and acacia were found to be 0.52, 0.5 and 0.53 mM/l respectively while that of TritonX-100 being 0.125 mM/l.

3.4. Measurement of Contact Angle

For measuring contact angle, contact angle meter, Data Physics, Germany, Contact Angle System (OCA-20) was used. A pump (Tarson Rockyvac 320) was employed to develop pressure (1 bar) for the purpose of nano-level surfactant solution dosing on a single strand of human hair.

Figure 3.3: Photograph of optical contact angle meter.

To avoid surfactant solution retention by the hair strand (adsorption on the surface and absorption in pores of each strand), it was washed with water and methanol after each set of reading. Surfactants are compounds which act in both lowering the surface tension of fluids as well as improving the stability of the nanofluid. Since, nanoparticles are prone to sedimentation after a few hours, so ultra-sonication was carried out each time before contact angle measurement. The ultra-sonication provides surface charge to the particle, which in turn creates a repulsive force between the nanoparticles, thus preventing particle agglomeration. The experiments were carried out each time with freshly prepared sample solutions within a few hours after nanofluid preparation.

3.5. Synthesis of silver nanoparticle

In this study, silver nanoparticle was formed by reducing aqueous silver nitrate using a strong reducing agent, sodium borohydride (chemical synthesis) on one hand and acacia (green synthesis), as mild reducing agent on the other. In the chemical synthesis route, freshly prepared $NaBH_4$ solution (100 mM) was added to 10 mL of solution containing shikakai or reetha (1 mM) and $AgNO_3$ (1mM), under continuous stirring to reach a constant $NaBH_4$ / $AgNO_3$ molar ratio of 2:1. Although the colour of the sample instantly changes from a pale yellowish (due to presence of shikakai) to dark reddish-brown indicating the formation of Ag nanoparticle, the reaction is allowed to proceed further for 1 hour, under continuous stirring for complete reduction at room temperature (37 ± 3 °C). Similarly, the colourless solution of reetha turns dark reddish brown, when Ag nanoparticle is produced from $AgNO_3$ on addition of $NaBH_4$ in the surfactant medium containing $AgNO_3$. While in the green synthesis route, $AgNO_3$ (150 mM) was added drop-by-drop in 10mL of acacia (1mM) and reetha solution (1mM) separately, until the acacia / $AgNO_3$ and reetha / $AgNO_3$ molar ratio of 4:1 and 11:1 was attained respectively. These ratios were found to be optimum leaving no unreacted $AgNO_3$ in the surfactant solutions. The colour of the sample turned from yellow-ochre (due to presence of acacia) to deep orange upon completion of nanoparticle synthesis. At room temperature (37 ± 3 °C), the complete reduction of $AgNO_3$ by acacia surfactant solution was completed in 6 hours while for reetha the same reduction took nearly 90 hours. So, the chemical route of nanoparticle synthesis was preferred over the green synthesis for reetha, mainly due to the longer time needed for the completion of reaction, for the latter procedure. It is interesting to note the colour change of reetha on addition of $AgNO_3$ at different time intervals. The solution is colourless initially, but it turns to light pink after 48 hours and then

to pale brownish colour after 90 hours and then it remains steady, indicating completion of reaction.

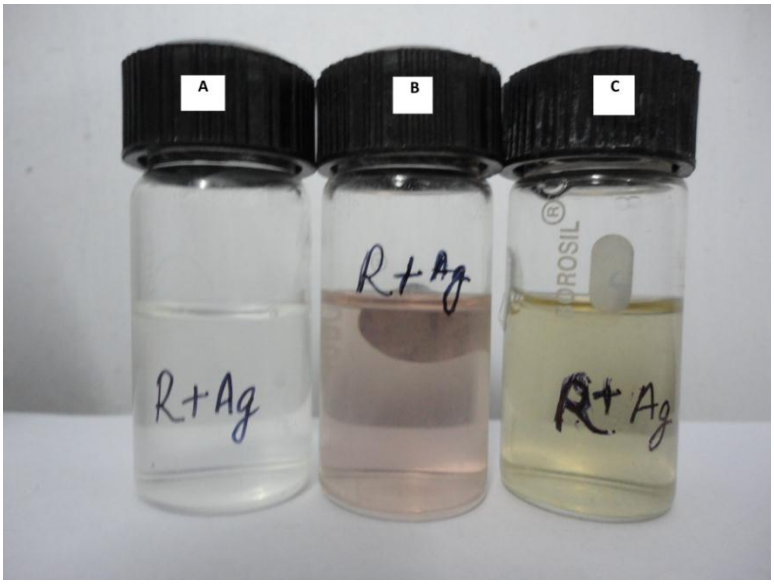


Figure 3.4: The colour change in reetha after addition of $AgNO_3$ at (A) t=0 mins, (B) t=48 hours and (C) t=72 hours.

3.6. Characterization techniques for silver nanoparticles

For measuring absorbance of silver nanoparticle in surfactant solution, UV 3600 (Shimadzu) was employed. The spectra were recorded at room temperature (37 ± 3 °C) using one-centimetre quartz cuvettes. While the absorption spectra provided solid evidence of nanoparticle formation and their growth kinetics, the size and shape of the resultant particles were elucidated with the help of dynamic light scattering (DLS), Nano ZS (Malvern Instruments) and from the images obtained in SEM analysis, respectively. Samples for scanning electron microscopy (SEM) operated at 20 KV, was prepared by drop-coating the Ag nanoparticle solutions onto glass slides. Samples were dried and coated with platinum before SEM analysis.

Chapter 4

WETTABILITY OF HAIR BY PURE SURFACTANT SYSTEM

4.1.Introduction

Surface tension exists between two dissimilar surfaces, which can either be at fluid-soild or even fluid-fluid interface. When two fluids are in contact with a solid surface, the equilibrium configuration of the two fluid phases (say air and water) depends on the relative values of the surface tension between each pair of the three phases. The surface tension acts upon its respective interfaces, and define the angle θ, at which the liquid contacts the surface. This is known as the wetting (or dihedral) angle of the liquid on the solid in presence of gas (air). Wetting fluid preferentially covers the surface of the solid. The origin of these surface tensions arises in the different strengths of molecular level interactions taking place between the pairs of fluids and different surfaces.

The measurement of contact angle can either be done by "dynamic contact angle" measurement, where the three-phase contact angle remains in motion with respect to the surface or by "static contact angle" measurement, where the three-phase contact angle is stationary. The measurement of dynamic contact angle (DCA) can be done by actually measuring the advancing contact angle (θ_A) during solid plate immersion and the receding contact angle (θ_R) during the emersion process. Generally, it has been observed that $\theta_A \neq \theta_R$, which has been accredited to various factors ranging from chemical heterogeneities to even roughness of the surface and this phenomenon is called contact angle hysteresis. While the measurement of static contact angle is done by using the goniometric technique, where a given liquid volume is dropped on a surface and its image recorded, from where the contact angle is calculated.

4.2 Result and Discussion

4.2.1 Solution behaviour of pure surfactants

Surface tension is the measure of energy required to increase the surface area of a liquid by unit area, caused due to an imbalance of intermolecular forces. Surface tension measurements were done for different concentrations of the three plant surfactants namely- reetha, shikakai and acacia, to get the minimum surface tension values at critical micellar concentration (CMC). Critical micellar concentration is the concentration beyond which further addition of surfactants do not reduce the surface tension properties by reducing interfacial tension, instead the surfactant molecules goes in the bulk phase to form micelles. The surface tension value gradually decreases with increasing surfactant concentration until

CMC value; beyond that concentration the surface tension remains constant. The change in surface tension values were plotted against log C in figure 4.1.

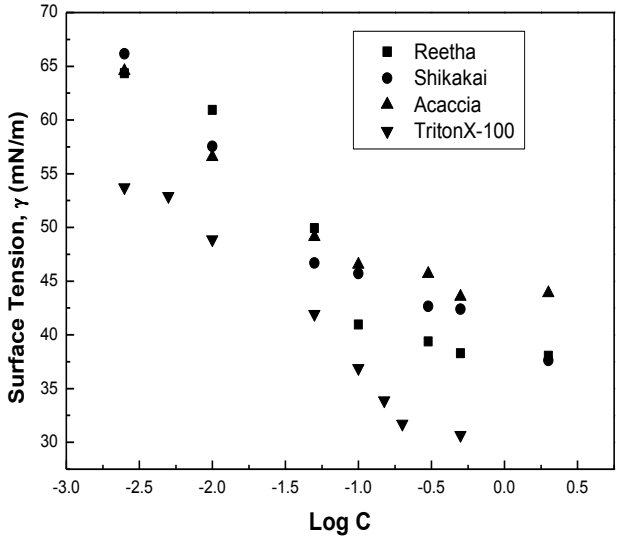


Figure-4.1: Change in surface tension with log C for reetha, shikakai, acacia and TritonX-100 solutions.

From figure 4.1, it is evident that the CMC values of all the plant surfactants lie very close to each other in range of 0.5 to 0.55 mM/l. While the CMC value of the non-ionic TritonX-100 is much lower being 0.125 mM/l. Then, quantitatively to get an idea about the adsorption of surfactants at the air-water interface, Gibb's surface excess equation was used to calculate the surface excess values as well as minimum surface area occupied per molecule, by using the following formulae:

$$\Gamma = - \frac{1}{n \times 2{,}303\, R\, T} \frac{d\gamma}{d\log C} \qquad (1)$$

$$A_{min} = \frac{1}{N_A\, \Gamma_{max}} \qquad (2)$$

where, Γ is surface excess in mole/m^2, A_{min} is surface area per molecule in nm^2, R is universal gas constant (8314 m^3 Pa/kg mole K), T is absolute temperature and N_A is Avogadro number (6.023×10^{23}). The value of n is 1 for non-ionic surfactant, 2 for 1:1 ionic surfactant and 3 for zwitterionic surfactant. Generally, to calculate A_{min}, Γ_{max} is approximated as Γ, for places where linear dependence between surface tension and log C exists. The value of dγ/dlogC was obtained from the slope of the plot of surface tension vs.

log C, measured at a constant temperature of 298 K. The experimental values for surface tension at CMC (γ_{CMC}), CMC, surface excess and molecular areas for three surfactants are given in Table 1.

Table-4.1: Surface tension at CMC (γ_{CMC}), CMC, surface excess (Γ_{max}) and molecular areas (A_{min}) for three surfactant solutions.

Surfactant	γ_{CMC} (mN/m)	CMC (mmol)	Exp Γ_{max} (mole/m^2) * 10^6	Exp A_{min} (nm^2)
Reetha	38.293	0.5	2.462	0.674
Shikakai	42.382	0.52	2.307	0.719
Acacia	43.562	0.53	1.939	0.8560

From Table 1, it is evident that reetha has more amount of molecules present at the interface followed by shikakai and acacia. From A_{min} we can get an idea about the packing of surfactant molecules at the air-liquid interface. A_{min} is lowest for reetha followed by shikakai and acacia, which implies that reetha, has more adsorption density than the others.

4.2.2 Wettability of human hair

Wetting or wettability is the process by which a fluid displaces another from the surface of a material. Commonly wetting can be categorised under three distinct heads, namely- spreading wetting, immersional wetting and adhesional wetting [Rosen, M. J. Surfactant and Interfacial Phenomena; Wiley- Interscience: New York, 2004].

Spreading wetting is the actual process when a liquid spreads on a solid substrate or material. Contact angle gives a measure of the surface wettability. When contact angle is 0°, it said to be complete wetting i.e, solid has strong affinity towards the liquid and when contact angle is 180°, it is said to be non-wetting, i.e, solid has no affinity towards liquid. But these are ideal cases and are not found in nature, whereas in actual, contact angle lies between 0° and 180°.

Virgin untreated hair was measured first and a value of 105° was obtained for ultrapure water. The values obtained experimentally (104 ± 5º) nearly agree with the values measured (103± 4º) by Lodge et al., (2006). Next the hair strands underwent alcohol wash, which lowered the contact angle of hair significantly from 104º to 87º. Virgin hair is hydrophobic in

nature [Baghdadli et al., 2008; C.R. Robbins, Chemical and Physical Behavior of Human Hair, 4th ed., Springer, New York, 2002; Wortmann et al., 2010] but the surface of alcohol treated hair shows increases wettability than untreated hair. This change of hair nature can be explained from the theory that when hair is treated with alcohol, it deposits on the hair surface and the molecules orient themselves in such a manner so that the anionic groups (OH^-) are towards the hair surface and the cationic groups ($CH_3CH_2^+$) are projected outwards. Thus, high energy cations might be held responsible in decreasing the contact angle and increasing its wettability. But, arbitrarily no definite conclusions can be drawn about the decrease in contact angle of hair from the above stated chemical interactions, since it cannot be proven, without studying the effects of individual chemical component on hair, a task which is easier said than done. Also, as the hair was rinsed with water after the alcohol wash, so the possibility of any alcohol molecule remaining attached to the hair surface is slim. This can be explained better by the theory proposed by Lodge et al., 2006, that that the contact angle of treated hair is undeniably characteristic of the wetting properties of the wetting agent itself [Lodge et al., 2006]. The theory only holds firm when the effect of wetting agent dominates the wetting properties of the fiber, (i.e human hair, in this case).

The contact angle decreases sharply with increasing concentration of surfactants and then becomes nearly steady after reaching CMC value. The change in sessile drop contact angle on a single of hair strand was studied and plotted in figure 4.2.

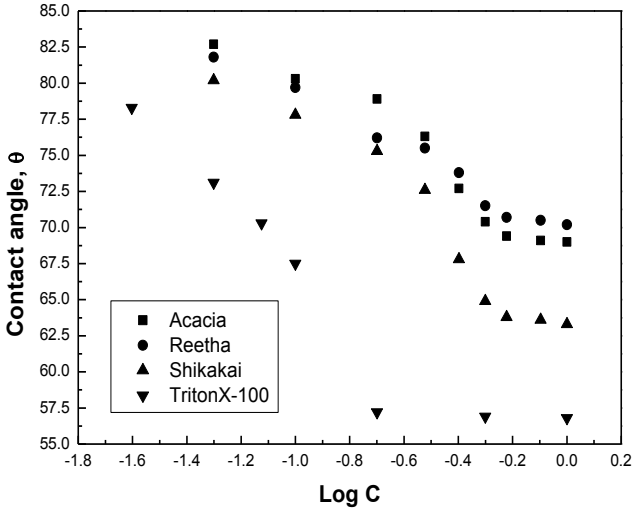


Figure-4.2: Change in contact angle with change in log C for pure reetha, shikakai, acacia and TritonX-100 on hair.

It can be clearly seen from figure 4.2, that there was a gradual decrease in contact angle with increasing surfactant concentration until 0.5 mmol/L (log C = -0.3) for each of the three pure plant surfactants, namely reetha, shikakai and acacia, beyond which there was no further reduction of contact angle with increasing surfactant concentration. The contact angle changes from 87° (pure water) to 57° with increasing concentration of TritonX-100. Similarly, for shikakai, reetha and acacia the change is from 87° to 64°, 70° and 71° respectively. The contact angles are similar for reetha and shikakai, with a slightly lower value for acacia below CMC. Lesser the contact angle, greater is the wetting phenomena. So from Figure 4.2, it can be concluded that among plant surfactants, shikakai has the highest wetting property, while reetha and acacia both has nearly equal wetting tendency for the same amount of concentration of each surfactant and also that the wettability of hair is directly dependent upon the surfactant concentration, up till CMC value.

4.2.3 Adsorption at solid-liquid and liquid-air interface

In this case, no linear relationship could be established between cosine of contact angle and surface tension, a linear relationship has been found to exist between adhesion tension ($\gamma_{LG}\cos\theta$) and surface tension (γ_{LG}), similar to those demonstrated by other researcher's [Szymczyk et al., 2006; Chaudhuri and Paria, 2009; Zdziennicka. A, 2009] empirical formula:

$$\gamma_{LG}\cos\theta = a\gamma_{LG} + b \qquad (3)$$

where, a and b are constants. The value of 'a' depends on the solid surface property. The values of 'a' and 'b' for three different surfactant are given in table 2.

Table-4.2: Values of 'a' and 'b' for three different surfactants.

Surfactant	A	b
Reetha	-1.92	85.84
Acacia	-1.75	90.99
Shikakai	-2.01	107.52

Combining and rearranging the Young's and Gibb's equation gives the following correlation:

$$\frac{\Gamma_{SG}-\Gamma_{Sl}}{\Gamma_{LG}} = \frac{d(\gamma_{SV}-\gamma_{Sl})}{d\gamma_{LG}} = \frac{d\gamma_{LG}\cos\theta}{d\gamma_{LG}} \qquad (4)$$

where, Γ_{SG}, Γ_{Sl}, Γ_{LG} represents the surface excess of surfactants at respective interfaces γ_{SV}, γ_{Sl}, γ_{LG} represents the interfacial tension at respective interfaces and θ being the contact angle between the solid-liquid interface. Taking Γ_{SG}=0, from the equation (4) it can be explained that the plot between surface tension and adhesional tension also gives the ratio between surface excess of solid-liquid and liquid-air interface as shown in Figure 3.

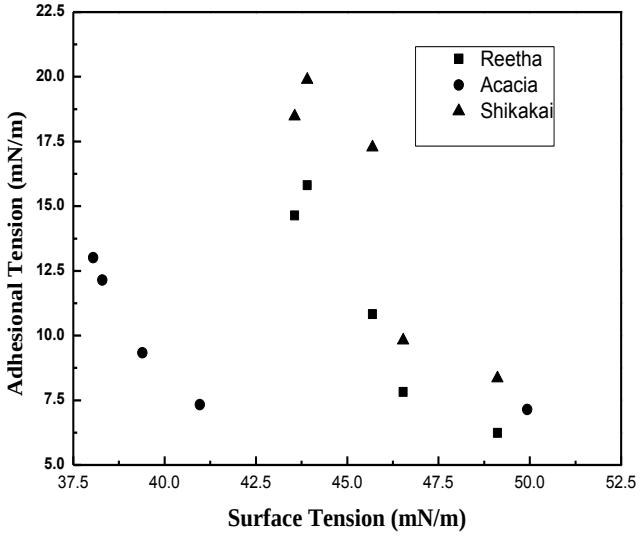


Figure 4.3: Variation of adhesional tension with surface tension for reetha, shikakai and acacia on hair surface.

The value of interfacial surface tension between solid and liquid, Γ_{sl} was obtained by putting the value of 'a' in equation 4, for the different surfactants. Γ_{sl} values obtained for reetha, acacia and shikakai were (mole/m^2), respectively. So, we can conclude that there is no equal adsorption at solid-liquid and liquid-air interface, which is evident from unequal Γ_{SL} and Γ_{LV} values. The unequal adsorption at the solid-liquid and liquid-air interface may be attributed to the very small contact time (~5 sec) between the fluid and hair, which prevents complete adsorption of surfactants on hair. Various other factors can be responsible for the unequal adsorption at the solid-liquid and liquid-air interface. The porosity in hair refers to its ability to absorb moisture. Generally damaged hair has no cuticular cover which makes it highly porous. The porous hair can easily absorb moisture and other chemicals and can get easily damaged. So, the water small water droplet gets absorbed in the hair before equilibrium wetting can be achieved. Also, due to the small size of the water droplet, evaporation can occur rapidly even before equilibrium adsorption can occur. The error in

calculation due to the presence of impurities on hair cannot also be completely ruled out. These are the probable casues for unequal adsorption at the solid-liquid and liquid-air interface and the exact nature cannot be ascertained.

4.2.4 Work of adhesion on hair

Work of adhesion measures the interactive forces between two different phases (solid and liquid), which not only depends on the surface tension but also on the contact angle. The solid–solution interfacial tension fulfils the condition:

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - W_A \quad (5)$$

where, W_A is the work of adhesion of the liquid to solid surface, which can be treated as the sum of two components, apolar (Lifshitz–van derWaals),W_A (apolar), and polar, W_A (polar), interactions across solid–liquid interface.

Using Young's equation another relation can be established as:

$$W_A = \gamma_{LV} (\cos \theta + 1) \quad (6)$$

Dependence between the adhesion works (W_A) of the aqueous solutions of surfactants to hair is plotted against Log C in figure 4, using the equation (6).

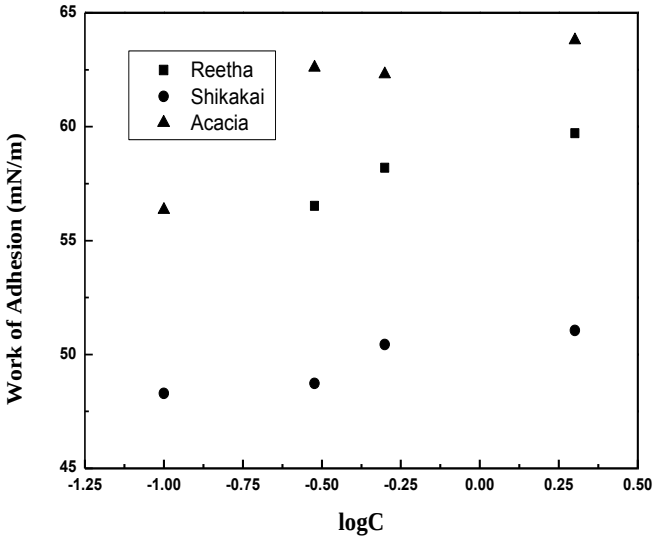


Figure 4.4: Change of work of adhesion with change in log C for for pure reetha, shikakai and acacia on hair.

From Figure 4.4, it is evident that with increasing concentration the work of adhesion increases for all the three surfactants. This occurs due to the increased wettability of hair, after the alcohol wash.

4.3. Conclusion

The decrease in contact angle with increasing surfactant concentration follows a trend similar to that of the respective surfactant surface tension properties. The wettability of hair generally depends on the nature of hair quality rather than on different ethnicities. The contact angle of water on virgin untreated hair is found to be 104±5°, which has been found to be the same for all the ethnicities. But, the treatment of hair with alcohol reduces the contact angle significantly from 104° to 87° respectively. The decrease in contact angle also occurs for damaged or chemically treated hair as found by Lodge et al., 2006. Unequal adsorption takes place at the solid-liquid and liquid-air interface. Generally, with increasing surfactant concentration, the free energy of wetting becomes more negative indicating that the process is thermodynamically favoured for all the surfactants.

Chapter 5

SYNTHESIS OF SILVER NANOPARTICLE

5.1.Introduction

The applicability of nanoparticles in the field of science and technology has generated immense interest among various groups of researchers. Metal nanoparticles are intensely studied due to their unique optical, electrical and catalytic properties. To utilize and optimize chemical or physical properties of nano-sized metal particles, a large spectrum of research has been focused to control the size and shape, which is crucial in tuning their physical, chemical and optical properties. The proliferation of nanotechnology has opened up new avenues for the synthesis of nanostructures with well-defined compositions, shapes, and sizes. The commonly used physical and chemical methods for nanoparticle synthesis are plagued by several problems ranging from disposal of toxic solvents or additives in the environment to being very energy intensive (i.e., due to stringent conditions). So, compared with conventional methods, bioreduction of salts of silver (using plant and micro-organisms) has shown promising results by being able to produce stable NP, which are both cost-effective and environment friendly. The stimulus provided by green synthesis has led to the biosynthesis of Ag [Krishnaraj et al., 2010], Au [Kumar and Yadav, 2009], Pd, TiO_2, CdS, etc. Generally biosynthesis of Ag NP is carried out at room temperature by using plant extracts or organisms, which results in low reaction rates and conversion of Ag ions. So, there persists a need for the rapid biosynthesis of Ag NP which could overcome the problems posed due to low conversion rates. By understanding the mechanism of green synthesis of Ag NPs by rapid bioreduction of silver ions, the transition from laboratory scale production to industrialization of the biosynthetic technique might become possible in the near future. The interest shown towards the application of biogenic silver nanoparticle has been tremendous and its anti-microbial properties are well established [Singhal et al., 2011; Fayaz et al., 2010; Prasad et al., 2011; Marimuthu et al., 2011; Sintubin et al., 2011; Sharma et al., 2009]. Application of silver nanoparticle in catalysis, sensors and medicine typically depends on the size and composition of the nanoparticle.

5.1.1. Green synthesis of silver nanoparticle

The soaring environmental concerns had prompted researchers to look for alternative methods for the synthesis of nanomaterials. Biosynthesis of nanoparticle by employing biological systems such as bacteria, fungi and plants has been coined as “green chemistry” or “green synthesis”. Many reports have been published about the biogenesis of silver nanoparticles using several plant extracts like gum kondagogu (*Cochlospermum gossypium*)

[Vinod et al., 2011], *Camellia sinensis* [Kamal et al., 2010], *Chenopodium album* [Dwivedi and Gopal, 2010], *Jatropha curcas* [Bar et al., 2009; Bar et al., 2009], *Acalypha indica* [Krishnaraj et al., 2010]. Besides these, black tea leaf extracts [Begum et al., 2009], banana peel extract [Bankar et al., 2010], *Cacumen platycladi* extract [Huang et al., 2011], geraniol [Safaepour et al., 2009], extracts from medicinal plant of basil (*Ocimum sanctum*) [Ahmad et al., 2010] has also been utilised to synthesise silver nanoparticles. The synthesis of silver nanoparticle has also been done using bacteria and bacterial isolates offers the benefits of being environmental friendly and scale-up of large scale industrial production. Among the many micro-organisms that has been employed *Brevibacterium casei* [Kalishwaralal et al., 2010], *Geobacillus stearothermophilus* [Fayaz et al., 2011], *Shewanella oneidensis* [Suresh et al., 2011], *Bacillus sp.* [Pugazhenthiran et al., 2009], *Escherichia coli* (S30, S78), *Bacillus megaterium* (S52), *Acinetobacter sp.* (S7) and *Stenotrophomonas maltophilia* (S54) [Zaki et al., 2011]. Krishnaraj et al., (2010) used leaf extracts of *Acalypha indica* to reduce silver nitrate and the absorption peak at 420 nm in UV–vis spectrum confirmed the formation of silver nanoparticle. Ahmed et al., 2010, explained that the conversion of Ag^{+} to Ag^{0} occurs due to the enol formation of luteolin and rosmarinic acid (figure-5.1).

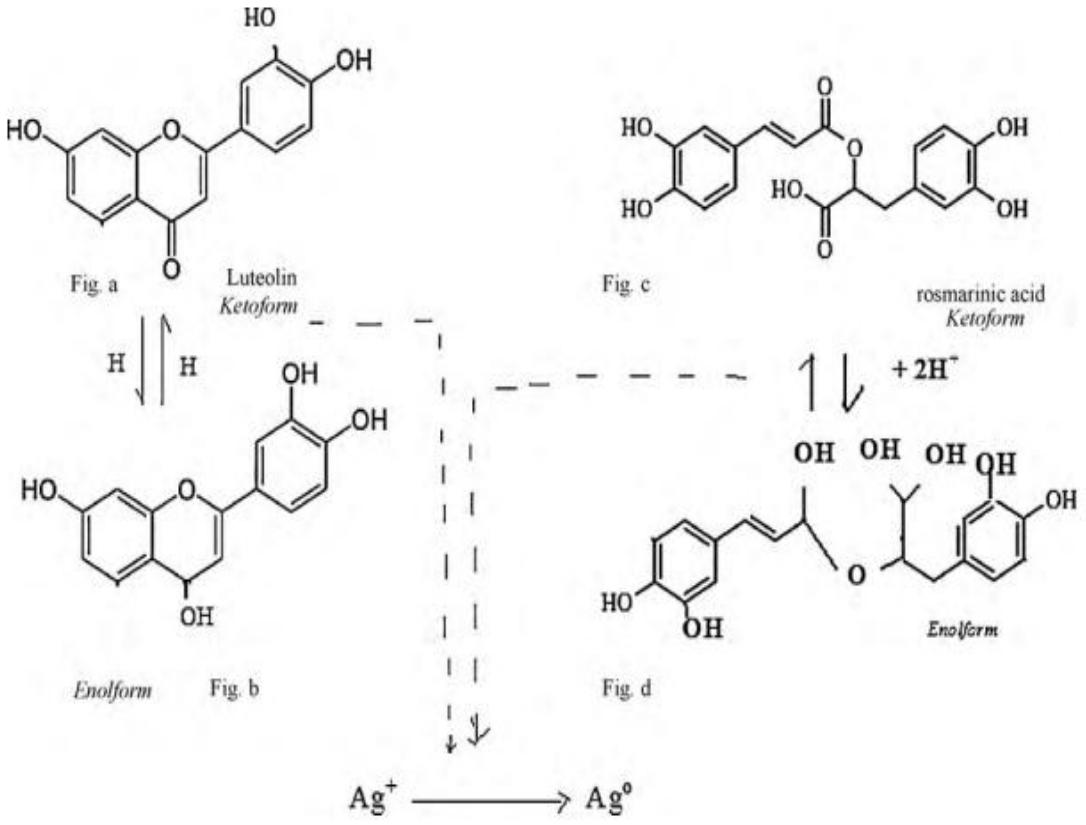


Figure 5.1: Mechanism of biosynthesis of Ag nanoparticle [Ahmad et al., 2010].

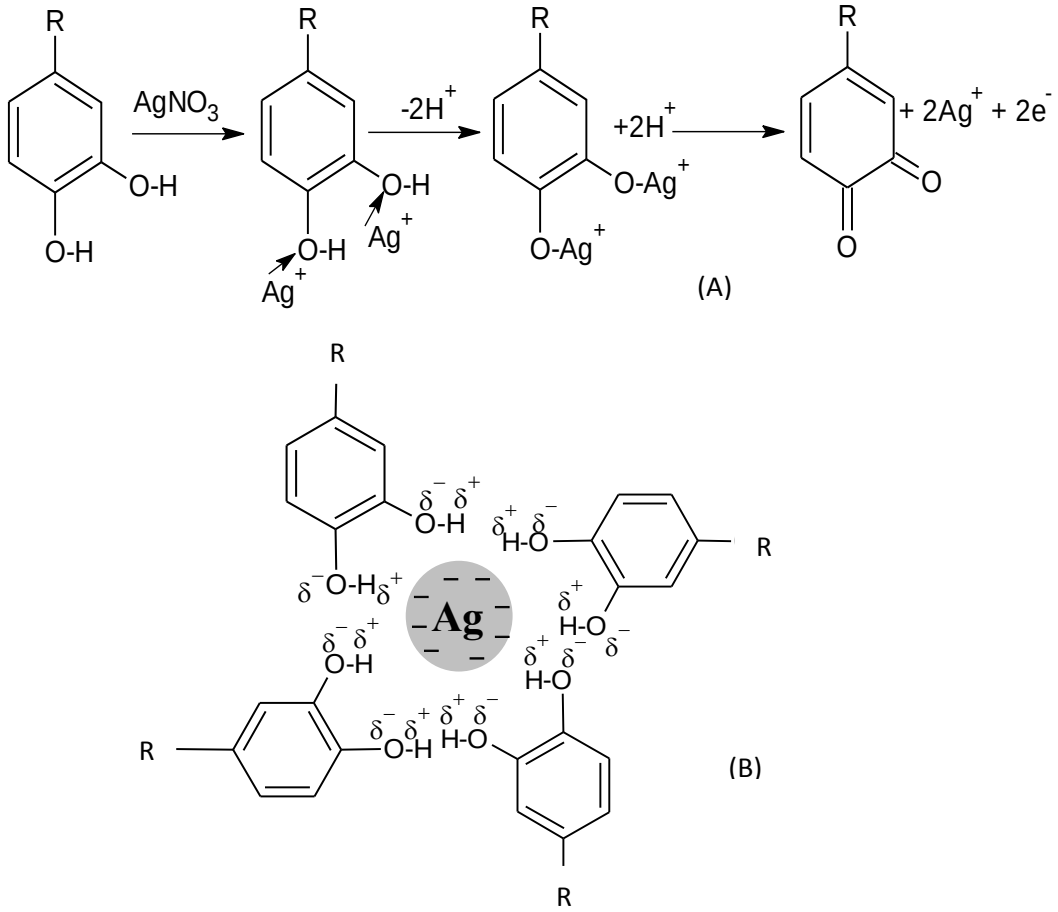


Figure 5.2: (A) General scheme of reaction mechanism of nanoparticle synthesis. (B) Control of formed nanoparticle size.

The formed silver nanoparticle attacks the hydroxyl group and the silver ion replaces hydrogen from the hydroxyl group (figure-5.2 (A)). The nascent hydrogen itself a strong reducing agent reduces Ag^+ to Ag^0, whiles itself getting oxidesed to H^+. The hydrogen ion further attacks the $–O\text{-}Ag^+$ bonds and forms stable hydroxyl molecules. The formed nanoparticle are stabilised by the overall structure attained by the surfactant molecule after completion of the reaction (figure-5.2 (B)). The overall reaction scheme is given below:

$$\mathbf{2Ag^+ + 2e^- \longrightarrow 2Ag^0}$$

or

$$\mathbf{2H^+ + 2e^- \longrightarrow H_2}$$

$$\mathbf{2Ag^+ + H_2 \longrightarrow 2Ag^0 + 2H^+}$$

5.1.2. Chemical synthesis of silver nanoparticle

Silver nanoparticles, with fixed size [Solanki et al., 2011, Shameli et al., 2010] and different shapes, like prism [Dong et al., 2010], sphere [Lu et al., 2011], etc can be synthesized by chemical reduction of silver nitrate with sodium borohydride reducing agent, in different concentrations. Shameli et al., (2010) prepared spherical silver nanoparticle by adding freshly prepared $NaBH_4$ to $AgNO_3$ solution under continuous stirring till $AgNO_3/NaBH_4$ molar ratio of 1:4 was achieved. The increasing molar ratio of $AgNO_3/NaBH_4$, leads to smaller particle size and better dispersion. While another group of researcher varied molar ratio of $NaBH_4$ to $AgNO_3$ concentration (0.5-15), initial $AgNO_3$ concentration and also surfactant(SDS) concentration to study the size and dispersion of Ag NP in the solution [Song et al., 2009]. At low $AgNO_3$ concentration there is a weak absorption maximum of surface plasmon peaks and with increasing the $AgNO_3$ concentration, the intensity of the maximum plasmon peak increased, clearly indicating that increasing the initial silver nitrate concentration increased the formation of silver nanoparticle. The narrower the absorption peak, the better the degree of dispersion of nanoparticles. At $NaBH_4$ /$AgNO_3$ molar ratios of 2-5, the absorption peak became broad, while at molar higher molar concentration (10-15) of $NaBH_4$ /$AgNO_3$, the peak became narrow. This indicates that silver nanoparticles are better dispersed in the solution at higher concentration than at lower concentration. Also, it shows that $NaBH_4$ not only acts as a reducing agent but also as a stabilizer, which protects the aggregation of silver nanoparticle. Generally, surfactants act as capping agent, which prevents growth and aggregation of nanoparticle. At high SDS/$AgNO_3$ the absorption peaks are narrower, meaning better dispersion of silver nanoparticle when compared to low SDS/$AgNO_3$, which shows broader peaks meaning aggregation of silver nanoparticle [Song et al., 2009].

5.2 Result and Discussion

5.2.1 Biosynthesis of silver nanoparticle in Acacia medium

The fruit extracts of Acacia was utilised as mild reducing agent for the biosynthesis of silver nanoparticle from silver nitrate salt. Acacia has medicinal property [Krishnaraj et al., 2010] and it also acts as capping agent, which prevents aggregation of biogenically produced silver nanoparticle. The initial concentration of plant extract and silver nitrate plays an important role in controlling the rate as well size of the nanoparticle. But the major problems associated with biosynthesis of nanoparticles are slow rate of production and the produced

nanoparticles are not monodispersible. In-situ production of silver nanoparticle has been done in acacia using silver nitrate salt within a few hours. The mechanism of reduction can be explained by studying the structure of Acacia (A) which is primarily composed of three triterpenoid saponins proacasiaside-I (B), proacaciaside-II (C) and acaciamine (D) [Garai and Mahato, 1997]. Acid hydrolysis done on structure (B) and (C) showed that both the saponins are acacic acid lactone disaccharides, while proacasiaside-I (B) contains two glucose units; the other proacaciaside-II (C) contains a glucose and a terminal arabinose sugar unit each. Acaciamine (D) is mainly composed of L-arabinose as the terminal sugar which is linked to NHAc-Glc bound to the acacic acid lactone. The probable cause of conversion of Ag^{+} to Ag^{0} occurs mainly due to the reduction of $AgNO_3$ by the five member keto group and the various sugar molecules present in the acacia structure (figure-5.3). The keto group is highly unstable since three of its carbon atoms are in the ring structure, so to get a stable linear structure it is readily oxidisable, and in turn it reduces the silver salt. Sugar molecules can act as mild reducing agent since the aldehyde group of sugar can be oxidized to form a carboxylic acid group, or in the presence of a base, a carboxylate ion.

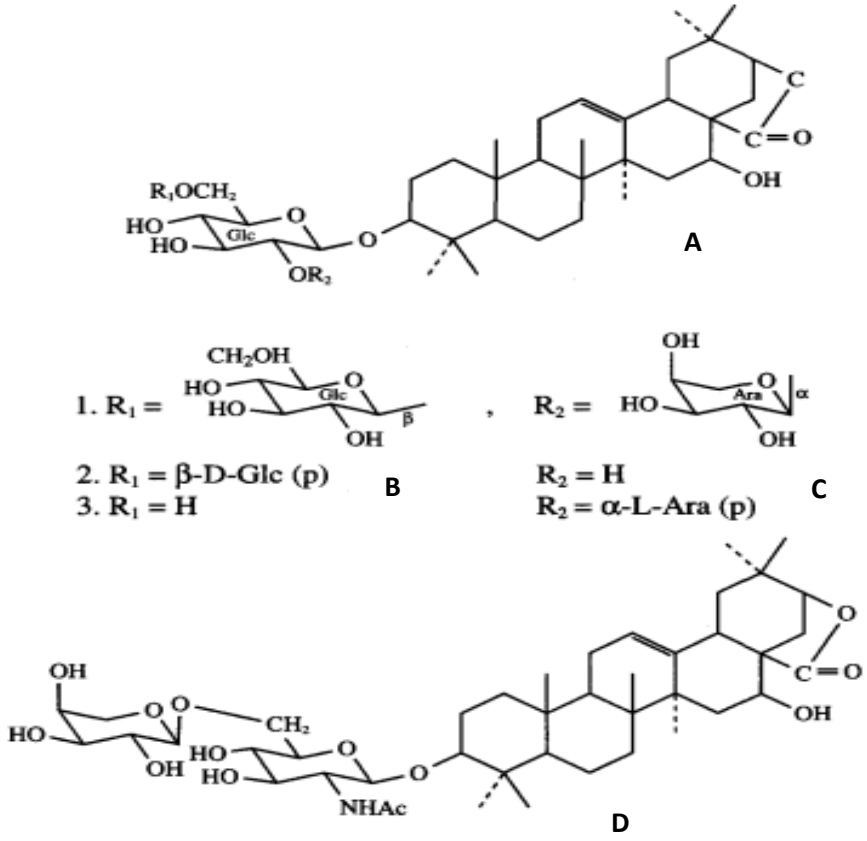


Figure 5.3: Structure of Acacia (A) and its three chief triterpenoid saponins proacasiaside-I (B), proacaciaside-II (C) and acaciamine (D) [Garai and Mahato, 1997].

At first, different concentration of $AgNO_3$ was added to acacia (1mM), ranging between the molar ratios of $AgNO_3$: acacia from1:1 to 1:6. It was then incubated in the dark for the reaction to proceed, reducing the chances of photoreduction of $AgNO_3$. Then by employing spectroscopic analysis, it was found out that ratio of 1:4 of $AgNO_3$: acacia is optimum, leaving no unreacted $AgNO_3$ in the surfactant solution. After the completion of the reaction, the ratios ranging between 1:1 to 1:3 of $AgNO_3$: acacia solution (1mM), was found to contain excess silver nitrate in the nanofluid, which was visually confirmed by the precipitation reaction on the addition of sodium chloride salt. To ascertain the rate of reaction with respect to time the absorption spectra of the silver nanoparticle synthesis was recorded at different time intervals and the corresponding spectra are shown in figure 5.4.

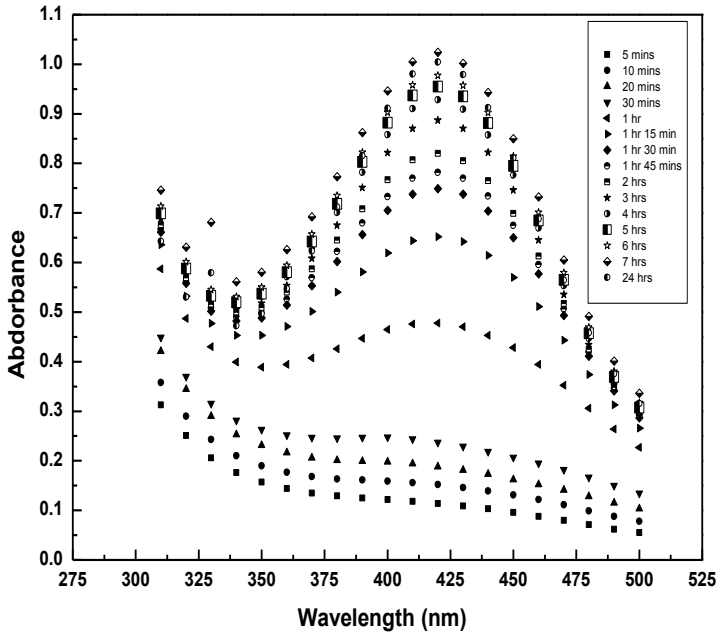


Fig 5.4: UV-Vis Absorption spectra of Ag nanoparticle formation in acacia solution at different time intervals.

From Fig. 5.4, it could be observed that the absorption maxima scanned by UV–vis spectra, at the wavelength of 300–500 nm in Shimadzu UV-3600 spectrophotometer gave a distinct single peak at 420 nm, on reduction of $AgNO_3$ by using acacia solution. A gradual increase in the intensity of the nanoparticle peak with increasing reaction time from 5 min to 6 hr, indicates the slow progression of Ag^+ to Ag^0 reaction. No significant change is observed between 6 hours to 24 hours' time interval suggesting the completion of reaction in 6 hours.

5.2.2 Chemical synthesis of silver nanoparticle in Reetha and Shikakai medium

The chemical synthesis of silver nanoparticle is achieved by the reduction of sliver salt (generally $AgNO_3$) by a reducing agent, in presence of a stabiliser, which controls the size of the nanoparticle and prevents it agglomeration. The reduction of $AgNO_3$ was carried by sodium borohydride ($NaBH_4$), a strong reducing agent in surfactant (reetha or shikaki) medium. Unlike acacia, shikakai and reetha are unable to reduce $AgNO_3$ to Ag NP, within hours. The reason attributed to their inability can perhaps be explained by studying the structural composition of shikakai (figure-5.5) and reetha (figure-5.6).

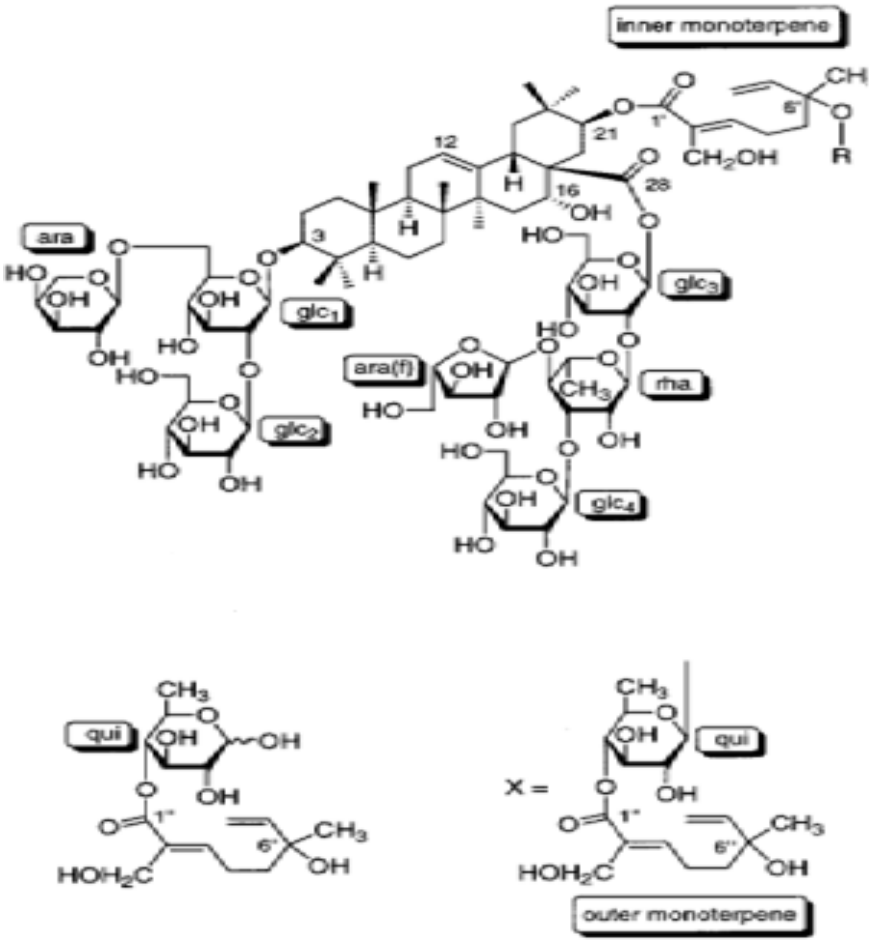


Figure-5.5: Structure of Shikakai [Tezuka et al., 2000].

Shikakai broadly consists of four monoterpenoids [namely- menthiafolic acid, a mixture (1:1) of (6S)- and (6R)-menthiafolic acid 6-O-β -D-quinovopyranoside, and a mixture (2:1) of two diastereomers of 3,6-epoxy-2-hydroxymethyl-6-methyl-7-octenoic acid and a mixture (1:1) of (2E)-6-hydroxyl-2-hydroxymethyl-6-methyl-2,7-octadienoic acid 6-O-β-D-quino-vopyranoside] and five prosapogenins [namely- acacic acid 3-O-R-L-arabinopyranosyl(1-6)-

[β -D-glucopyranosyl(1-2)]-β-D-glucopyranoside, acacic acid 3-O-R-L-arabino-pyranosyl(1-6)-2-acetamido-2-deoxy-β-D-glucopyranoside, 3-O-β-D-xylopyranosyl(1-2)-R-L-fuco-pyranosyl (1-6)-[β-D-glucopyranosyl(1-2)]-β-D-glucopyranoside, acacic acid 3-O-β-D-xylopyranosyl(1-2)-R-L-arabinopyranosyl-(1-6)-2-acetamido-2-deoxy-β-D-glucopyranoside and acacic acid lactone 3-O-β-D-xylopyranosyl(1-2)-R-L-ara-binopyranosyl(1-6)-[β-D-glucopyranosyl(1-2)]-β-D-glucopy-ranoside] respectively. The reduction of $AgNO_3$ by shikakai does not take place even after one week of incubation time, since no sufficient reducing group is present as can be seen from the structure (figure-5.5). The carboxylic group (-COOH) present in the shikakai structure is an oxidising agent, which cannot reduce $AgNO_3$.

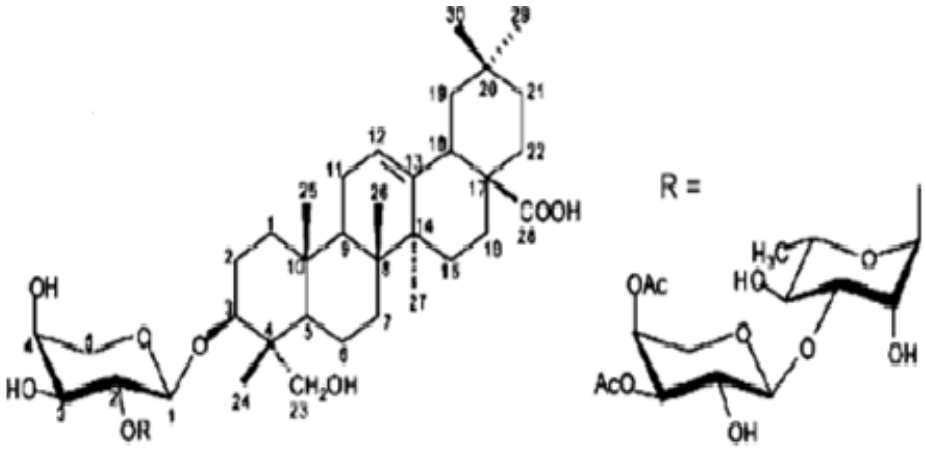


Figure-5.6: Structure of Reetha [Rao and Paria, 2009].

The structure of reetha is broadly composed of 13 different saponins namely-sapinmusaponin K, sapinmusaponin L, sapinmusaponin M, sapinmusaponin N, sapinmusaponin O, sapinmusaponin P, mukurozi-saponin G, hederagenin-3-O-(2-O-acetyl-β-D-xylopyranosyl)-(1-3)-α-L-rhamnopyranosyl-(1-2)-α-L–arabinopyranoside, hederagenin-3-O-(3-O-acetyl-β-D-xylopyranosyl)-(1-3)-α-L-rhamnopyranosyl-(1-2)-α-L rabinopyranoside, mukurozi-saponin E1, sapindoside B, sapindoside A and hederagenin-3-O-β-L-arabi-nopyranosyl-(1-3)-α- L -rhamnopyranosyl-(1-2)-β-L-arabinopyranoside [Huang et al., 2008]. The formation of silver nanoparticle from its salt takes place very slowly and is completed in about 90 hours' time (at 35° C). The primary alcohol group (-CH_3OH) present in the reetha structure (figure-5.6), although present in stable sp_3 hybridised state, can actually be held responsible for the slow conversion of Ag^+ to Ag^0, while the alcohol group is itself reduced to aldehyde in the process.

At first, surfactant (reetha or shikaki) solution (1mM) was taken to which $AgNO_3$ was dropped to achieve 1mM $AgNO_3$ concentration. Then $NaBH_4$ was added drop by drop in the solution so that the final molar concentration of $AgNO_3$: $NaBH_4$ becomes 1:2. The particle size is affected due to various parameters like initial $AgNO_3$ concentration, surfactant (capping agent) concentration, reaction temperature and also reducing agent concentration [Shameli et al., 2010; Song et al., 2009]. A high initial $AgNO_3$ concentration leads to faster reaction and increased silver nanoparticle synthesis. Higher concentration of capping agent and reducing agent leads to lower nanoparticle size, since agglomeration of nanoparticles is strongly inhibited. Higher temperature leads to quicker reaction which in turn leads to rapid synthesis of nanoparticles. The resulting nanoparticle synthesis from $AgNO_3$ by the reducing agent sodium borohydride in presence of surfactant (reetha or shikaki) occurs by the following given equation:

$$Ag^{+} + BH_4^{-} + 3\ H_2O \rightarrow Ag^{o} + B(OH)_3 + 3.5\ H_2$$

The reaction is instantaneous and the colour of the solutions depended on the concentration of added $AgNO_3$ solutions, surfactant type and its concentration, concentration of reducing agent among the other major factors. When nano-scale clusters of silver atoms are hit by light energy (photons), the free electrons of the surface atoms began to 'slosh' back and forth and create electron waves called surface plasmon. These electron waves are responsible for the production and release of light energy. The colour of the emitted light depends upon size and shape of the nanoparticles. The loosely bound electrons oscillates coherently with a frequency ω_p,

$$\omega_p{}^2 = \frac{4\pi N e^2}{m_e}$$

N = no of electrons in the plasma;

e = change of an electron;

m_e = effective mass of electron;

ω_p = oscillating frequency.

To ascertain the nanoparticle formation the absorption spectra was taken and the silver surface plasmon resonance bands were detected at around 406-420 nm (figure-5.2).

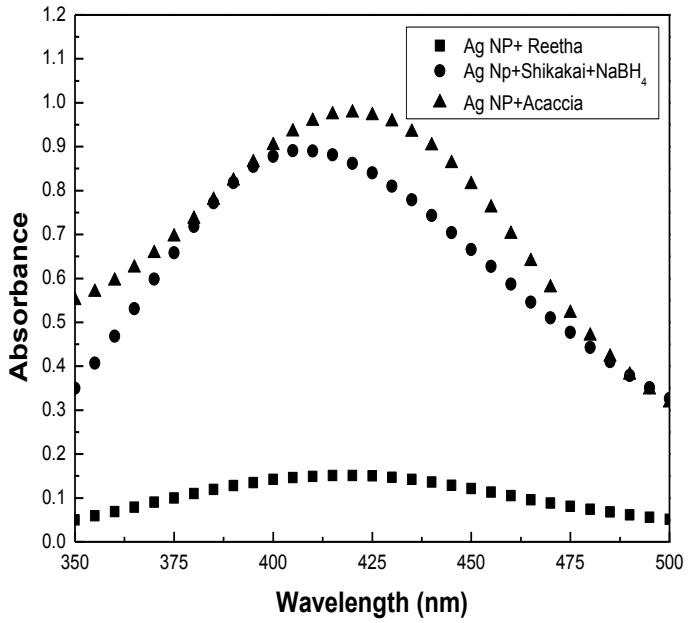
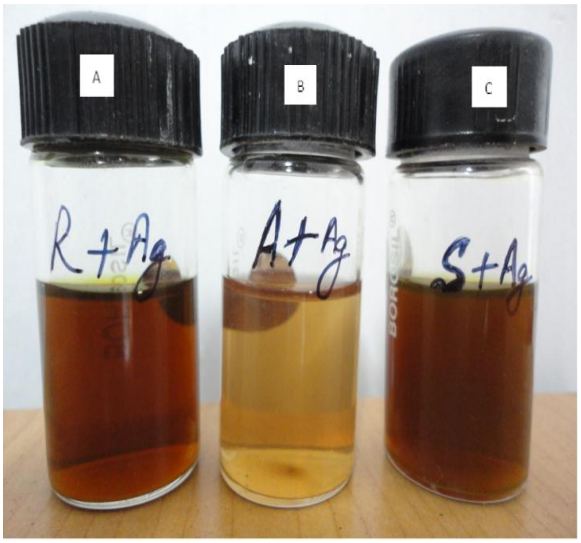


Figure-5.7: UV-Vis Absorption spectra of Ag nanoparticle formation in surfactant solution.



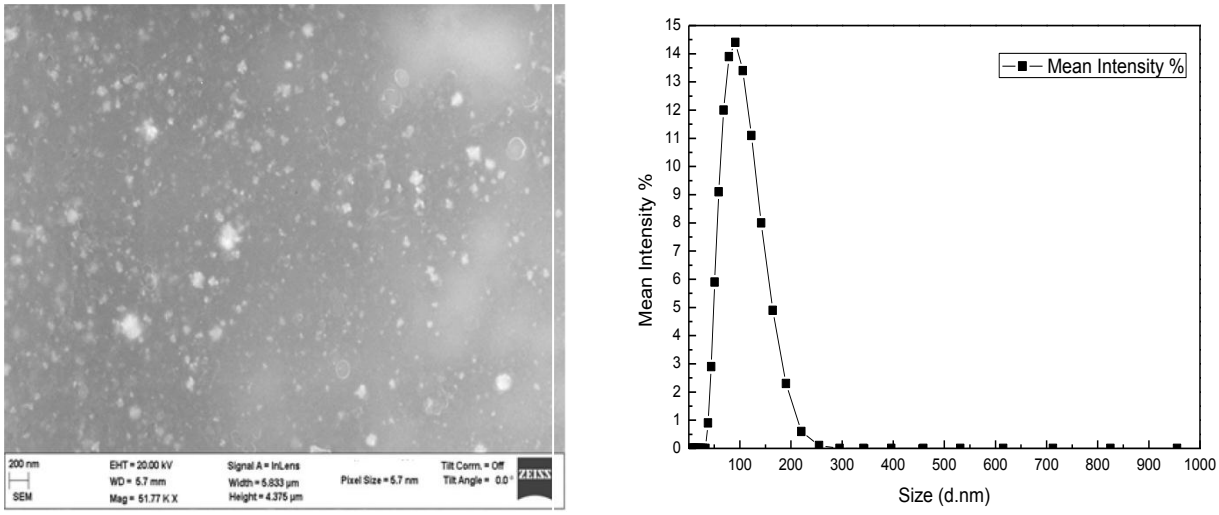
5.8 (a) 5.8 (b)

Figure-5.8: (a) 1 mM surfactant solution before nanoparticle formation [(A) Reetha (B) Acacia (C) Shikakai]; (b) Colour of samples after silver nanoparticle formation [(A) Reetha+$AgNO_3$+$NaBH_4$ (B) Acaccia+$AgNO_3$ (C) Shikakai+$AgNO_3$+$NaBH_4$] for 1mM $AgNO_3$ and surfactant and 2 mM $NaBH_4$.

The absorption peak of Ag NP was 406 nm in reetha, 418 nm in shikakai and 420 nm in Acacia. The excitation of surface plasmon by light is denoted as a surface plasmon resonance (SPR) for plasma surfaces. The colour of the samples (figure-5.8(b)) also shows a distinct difference in physical appearance, indicating that the nanoparticles produced are of different sizes, as established by the different absorption maxima obtained in figure 5.7.

5.2.3 Analysis of nanoparticle size by DLS and SEM

While the absorption spectra provide solid evidence of nanoparticle formation and their growth kinetics, the size of the resultant particles were elucidated with the help of dynamic light scattering (DLS). After 24 hours, the analysis of Ag nanoparticle formed by the reduction $AgNO_3$ by acacia was done using Nano Zetasizer, which gave the hydrodynamic size in the range of ~90nm. The sample was sonicated for 15 mins before performing measurement of size by DLS. According to thermodynamics, the minimization of total energy of the system leads to increased stability and every system has a tendency to achieve maximum stability. So, after the formation of sufficient amount of nucleate particle in the solution, the process of nucleation commences leading to the overall increase in particle size. The small particles coalesce to form larger particles by releasing energy. So, sonication is carried out to supply energy to the system which in turn provides surface charge to the particles, creating a repulsive force which hampers agglomeration.



(A) (B)

Figure-5.9: (A) Sem image of silver nanoparticle in Acaccia medium (1 mM concentration) (B) Measurement of Ag NP size in acacia solution.

Figure 5.9 (A), shows the SEM images of silver nanoparticle synthesised in 1mM concentration Acaccia medium, which acts as both reducing as well as capping agent. From the figure it is clear that the silver nanoparticle are almost spherical and uniform in size. The SEM images also supports the result obtained from DLS measurements (figure-5.9 (B)). It can be clearly seen from the above figure that silver nanoparticle has a tendancy towards agglomeration, so it is difficult to get separate discrete silver image.

5.2. Conclusion

The particle size depends on temperature, silver nitrate concentration, surfactant concentration and also kind of surfactant used. Sonication is carried out to increase the total energy of the system, so that the nanoparticles would not have a tendency to agglomerate, for which the overall particle size tends to remain low. The growth rate of particle has been found to change upto CMC concentration, above which the size almost remains constant. The presence of surfactant medium reduces the growth rate and thus the overall particle size tends to remain small compared to nanoparticle growth in non-surfactant medium. At high temperature and high initial concentration of $AgNO_3$, increased particle synthesis takes place when compared to reactions occuring at low temperature and low $AgNO_3$ concentration. The broad absorption peak indicates that the nanoparticles formed by the reduction of small quantity of $AgNO_3$ are not well dispersed in the surfactant medium and they have a tendency to agglomerate.

Chapter 6

WETTABILITY OF HAIR BY NANOFLUID

6.1. Introduction

Nanocoatings can modify the surface properties of the substrates, such as the roughness and the surface energy, while maintaining constant thermal properties. While coating of surfaces have gained prominence in various fields of study, along with it the importance of improving wettability by employing nanofluids has also emerged as an attractive alternative for those surfaces which cannot be modified easily. The additions of nanoparticles alter various properties of the base fluid like thermal conductivity, wettability, viso-elastic property, heat transfer coefficient, etc which play an important role in many key industries. The use of nanoparticles has not been limited to the major industries but it has created a niche in the cosmetic industry also. Nanoparticles have been employed to encapsulate the smell and enhance the wettability of any surface. In this present work natural surfactants (reetha, shikakai and acacia) were employed in which silver nanoparticle was dispersed to check the wetting behaviour of human hair, by using the static contact angle measurement technique. Also, silver nanoparticles have established as a strong anti-microbial agent which increases the shelf life of the surfactant concentration. The development of nanofluid technology is currently marked by various problems due to the lack of proper knowledge of the working mechanism of the nanofluids in conjunction with the difficulties in synthesising optimum suspensions.

6.2. Result and Discussion

6.2.1. Solution behaviour of nanofluid

Surface tension measurements were done for different concentrations of Ag NP in acacia as well as Ag NP in acacia and shikakai mixture. The parameters affecting the physical properties of nanofluids and surface wettability include the type of material, concentration, size and shape of nanoparticle along with the nature of the base liquid. Nanoparticles can effectively decrease the liquid-gas and solid surface tensions, by shifting the triple contact line and thus increases the wettability of the nanofluid. The transfer of nanoparticle from the bulk to the interface occurs mainly due to diffusional transfer and the subsequent attachments of the nanoparticle to the fluid interface are mainly governed by their hydrophobic/lipophilic character. Nanoparticles tend to transfer from the bulk solution to the interface, depending upon their wettability, which is generally responsible for changing the mechanical properties of the interfacial layers. So, this can be employed for the prevention of coalescence of drops and bubbles for emulsions and foams, while also having a stabilising effect on the solution.

The surface tension value gradually decreases with increasing concentration until CMC value; beyond that concentration the surface tension remains constant. The surface tension values of Ag NP in surfactant suspension (reetha, shikakai and acacia) shows a sharp decrease than the values exhibited by the surfactant in their pure forms. The change in surface tension values were plotted against log C in the figure-6.1.

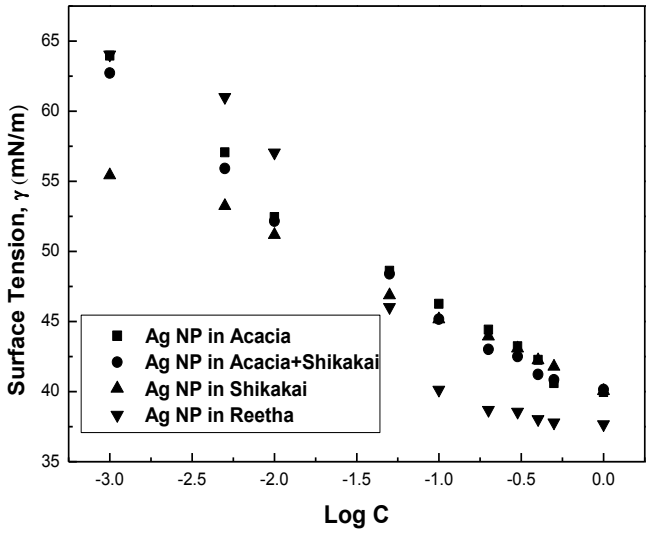


Figure-6.1: Change in surface tension with log C for Ag NP in Acacia, Acacia-Shikakai and Ag NP mixture, Shikaki-$NaBH_4$ and Reetha- $NaBH_4$.

From figure 6.1, it can be seen that the surface tension of acacia, reetha and shikakai at CMC are 43.5 mN/m, 38.6 mN/m and 42.4 mN/m respectively. Whereas the surface tension of Ag NP in acacia, reetha and shikakai at CMC are 39.96 mN/m, 37.8 mN/m and 40.01 mN/m. The nanoparticles itself have no effects on the interfacial properties, since they hardly reduce the surface tension. But, in conjuction with surfactant system they play an important role in changing the properties of the base liquid. Nanoparticles remain dispersed in the surfactant system, but with increasing the nanoparticle concentration the particles move towards the interface. So, with increasing the surfactant and nanoparticle concentration upto the CMC value the surface tension decreses apprecaibly. Then if the concentration of surfactant is increased above CMC it does not reduce the surface tension further. But, with the increase of nanoparticle concentration even above the CMC concentration of the surfactant, leads to a slight decrease in the surface tension values. This occurs due to particle diffusion from the bulk solution to the interface, but by increasing the amount of nanoparticle percentage, the process of surface re-organisation kicks in, mainly due to the excess transfer

of the nanoparticle to the interface. An irreversible transfer of nanoparticles occurs to the interface due to the continuous increase of the amount of absorption taking place at the interface. Above a certain amount of nanoparticle concentration, the exchange with the bulk is not very relevant relevant since a kinetic reversible process gains relevance.

6.2.2. Wetting behaviour of nanofluid on hair

Surface forces are very important for understanding both wetting and colloidal suspensions phenomena. The forces at play mainly arise due to interaction between phases and surfaces at a molecular level. The interactions between colloidal systems and interfaces are given by DVLO theory (Derjaguin–Landau–Vervey, and Overbeek). The liquid profile is thick away from the three-phase contact line but it gradually thins around the three-phase conatct line. The presence of nanoparticle near the three-phase contact line shifts the the contact line further, enabling dynamic wetting due to increase of disjoining pressure. Disjoining pressure has three important components: (molecular (Π_m), electrostatic (Π_e) and structural (Π_s)) [Sefiane et al., 2008]. Depending on the attractive or repulsive nature of the disjoining pressure, the calculated hamaker constant can either be positive (repulsive forces) or negative (attractive forces).

Disjoining pressure (II) = molecular (Π_m), electrostatic (Π_e) and structural (Π_s)

Each of the compnents can be calculated separately to determine the overall disjoining pressure. While DLVO theory explains the electrostatic (Π_e) and structural (Π_s) forces, the molecular component can be calculated by London–van der walls molecular interactions.

$$\Pi_m = \frac{A_h}{6\pi h^3}$$

A_h is a constant referred to as Hamaker constant and h is the liquid film thickness.

The deposition of nanoparticle at the solid surface could also be a possible cause for the observed increase in contact line shifting in the vicinity of the three-phase contact line. The deposition of nanoparticles allow the nanofluid to spread further due to the rolling-over of the contact line over the spherical nanoparticles. The effects hold true for lower particle concentration since at higher concentration the nanoparticles aggregate and forms a wedge at the three-phase contact line, which restricts nanofluid spreading.

We have used the nanofluid (Ag NP in acacia) for nano dosing in hair, which has dual advantage of increased wetting along with anti-microbial property. For a given volume of fluid, the spreading is increased if the contact angle becomes less. So, nanoparticles in fluid

suspension decreases the contact angle and thus aid in enhanced spreading of the nanofluid. The determination of nanofluid wettability can be done effectively by probing the individulal as well as combinational effects of environment, nature of base liquid, characteristic of nanoparticle and also the substrate material. The contact angle at first decreases with increasing concentration until 0.5 mmol/L (log C = -0.3) of surfactants but becomes steady after CMC is reached. The Ag NP sythesised by the chemcial reduction of $AgNO_3$ using $NaBH_4$ in reetha and shikakai medium has also been employed for doing wettability studies of the concerned nanofluid on the hair. Since synthesis of Ag NP in shikakai needs prolonged time, nearly upto 7 days, so we have grown Ag NP in acacia and mixed it with equimolar concentration of shikakai and studied its wettability on hair, which is shown in figure 6.2.

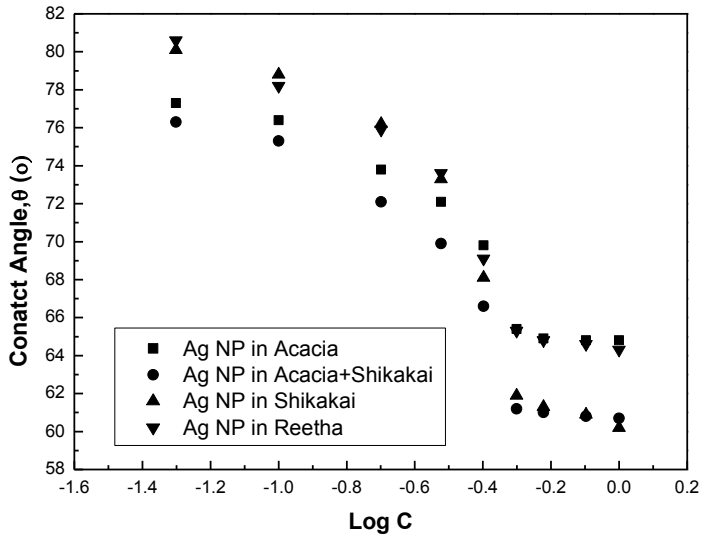


Figure-6.2: Change in contact angle with change in log C for Ag NP in Acacia, Acacia-Shikakai and Ag NP mixture, Shikaki-$NaBH_4$ and Reetha- $NaBH_4$.

From figure-6.2, it can be noticed that the contact angle of alcohol treated hair changes from 87° (pure water) to 70° with increasing concentration of reetha and upto 63° for shikakai. But, the presence of silver nanoparticle in the surfactant solution leads to a further increase in wettability of the surfactant on the hair. At CMC, the contact angle given by the Ag NP in acacia is 65°, nearly 6° lesser than that given by pure acacia solution which is 71°. The Ag NP in acacia and shikakai solution mixture gives a contact angle of 61°, which is even lower than that given by pure shikakai solution (64°) on hair. While the contact angle obtained at CMC was 62° and 64° respectively, for Ag NP formed by reducing $NaBH_4$ in shikakai and reetha. The "lubricating behaviour" of nanoparticle is similar to the

superspreading of surfactants over hydrophobic surfaces. Nanofluids improve the wettability mainly due to two phenomenon, namely- increase of structural disjoining pressure and reduction of friction due to nanoparticle adsorption on the solid surface. It is known that due to smaller nanoparticles a larger change in the contact angle is observed. As, the particle size increases the conatct angle increases upto a maximum concentration above which contact angle decreases with an increase of particle size. So, the wetting by nanofluids is a complex phenomenon depended on particle size, particle concentration, type and nature of surfactant used, nature of surface among many others.

6.3. Conclusion

The nanofluids has been employed to check the wettability of hair. The surface tension of the nanofluid is slightly lower than the surface tension of the base fluid. But, we get improved wettability of the nanofluid on hair compared to the pure surfactant. Also, its is important to note here that nanoparticles in the surfactant medium increases the shelf-life of the surfactant medium conisderably. It was seen that fungal attacks on surfactant solution is a common phenomenon. While reetha is attacked after only three days, shikakai has a slightly improved shelf life of 6-7 days while acacia can be stored for nearly 10 days. But on addition of nanoparticles the storage life of all the surfactants are increased and they are not prone to fungal attacks even after 21 days of storage.

Chapter 7

CONCLUSION AND SUGGESTION FOR FUTURE WORK

7.1. Conclusion

The results presented in chapters 4, 5 and 6 on the wetting behaviour of surfactants on hair, synthesis of silver nanoparticle and finally the wetting behaviour of nanofluid on hair can be summarized as follows.

Hair being hydrophobic in nature shows improved wettability on treatment with alcohol which increases the wettability by decreasing the contact angle. The wettability of hair is improved by the use of plant surfactants-namely reetha, shikakai and acacia. Although, these plant surfactants fail to achieve the wettability shown by TritonX-100 a synthetic surfactant, but they are comparatively cheaper, biodegradable and environmental friendly. The wettability of hair generally depends on the nature of hair quality rather than on different ethnicities. Also, it has been observed that the wettability of damaged and chemically treated hair is more compared to virgin untreated hair. The contact angle and surface tension values decrease with increasing surfactant concentration upto the CMC value. By increasing the surfactant concentration beyond the CMC value, no change in the values of contact angle and surface tension can be observed.

The synthesis of silver nanoparticle has been done by employing both chemical and biological methods. In the biogenic synthesis of silver nanoparticle acacia was used both as a mild reducing agent as well as capping agent. The reduction of $AgNO_3$ by using acacia solution gave a distinct single peak at 420 nm with the size of the silver nanoparticle being ~90 nm. The presence of surfactant medium reduces the growth rate and thus the overall particle size tends to remain small compared to nanoparticle growth in non-surfactant medium. The other surfactants, namely reetha and shikakai were unable to reduce $AgNO_3$ within hours and the reaction completion took many a days. For this reason $NaBH_4$, a strong reducing agent was employed for the synthesis of Ag NP in surfactant medium. The absorption peak of Ag NP was 406 nm in reetha and 418 nm in shikakai. The particles were spherical in shape and have a tendency towards agglomeration, as evident from broad UV-vis spectrum.

The decrease of interfacial tension and increase in cos θ value in presence of Ag NP for surfactants compared with equimolar concentration of pure surfactant solutions. The particle size increases the contact angle upto a maximum concentration above which contact

angle decreases with an increase of particle size. The wetting by nanofluids is a complex phenomenon depended on particle size, particle concentration, type and nature of surfactant used, nature of surface among many others. The nanofluid has dual advantage of increased wettability and anti-microbial property. The plant surfactants are prone to fungal attacks and thus cannot be stored in solution for long periods of time. The addition of silver nanoparticle increases the shelf life of the surfactant solution quite appreciably.

6.2. Suggestions for future work

This work can be further channelized in different avenues, namely-

(1) The work conducted has been done using static contact angle measurments, similar study can be done using dynamic contact angle measurement and check the validity of the results obtained for different surfactants.

(2) The work has been carried out on virgin hair of Caucasian origin. Similar studies can be done using different hair conditions and on hairs belonging to different ethnic groups and co-relate between the obtained results.

(3) The synthesis of other nanoparticles and their wettability study on hair can be conducted.

(4) The effect of nanoparticle size and concentration of reactants can be undertaken.

(5) The anti-microbial property of silver being well established, it can be used to improve the shelf-life of any given surfactant. A comprehensive study is lacking about the mechanism of the given process.

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Research Publication

To be communicated

- Krishnendu Chatterjee and Santanu Paria. **"Wettability of hair using natural and synthetic surfactants in presence of silver nanopaticles as additive".**
- Krishnendu Chatterjee, Sreerupa Sarkar and Santanu Paria. "**Review study on biomedical application on core/shell nanoparticle".**

Selected for conference

- Krishnendu Chatterjee and Santanu Paria. **"Wetting of PTFE surface by pure plant surfactant solution".** Chemcon-2011 (M.S.R.I.T, Bangalore), December 27-29, 2011.
- Krishnendu Chatterjee and Santanu Paria. **"Wettability of hair using natural surfactants and silver nanoparticle as additive".** Recent Advances in Chemical and Environmental Engineering-2012 (NIT, Rourkela), January 20-21, 2012.